



Ecotoxicological effects of polyacrylate, acrylic acid, polyacrylamide and acrylamide on soil and water organisms

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Summary

Some fertilizers can contain polymers composed of acrylamide (AMD) or acrylic acid (AA). Cross-linked polyacrylamides (PAM) and polyacrylates (PAA) can absorb huge amounts of water, thus belonging to the class of Superabsorbent Polymers (SAP). SAPs are available under various commercial formulations used for improving the water retention capacity of the soil or used as coating substance to promote a controlled release of nutrients. PAMs having a linear structure are in turn water soluble and are commonly used as flocculants/coagulants for accelerating liquid-solid phase separation in many industrial domains. To date, no fertilizer containing PAAs or PAMs in order to improve the water retention capacity is authorized in Switzerland, but there are some authorized fertilizers originating from recycling processes where flocculants have been used and therefore linear PAMs are supposed to be present as residuals. As polymers are not covered by main chemical regulations for environmental risk assessment, knowledge about their ecotoxicological effects is still limited. Based on a request by the Swiss Federal Office for Agriculture (FOAG), the Ecotox Centre composed this report, which aims at (i) summarizing the state of the art about the effects of PAMs and PAAs to soil and water organisms, when applied with fertilizers and (ii), if data availability allows, deriving critical values for use in risk assessment.

The first part of this report focused on the properties, environmental behaviour and environmental release of linear PAMs and cross-linked PAMs/PAAs. Both polymer classes adsorb strongly to soil particles and degrade slowly (<10 % per year) and are therefore persistent in the soil. Degradation is generally assumed not to lead to the formation of toxic monomers, such as AMD, although a few studies observed its release from PAM under either UV exposure or high temperatures. Better knowledge about degradation products is therefore required. Transfer to water is expected to be low. Predicted Environmental Concentrations (PEC) derived for the soil compartment ranged from 0.1 to 26.6 mg/kg for linear PAMs contained in sludges used as soil amendments, and from 3 to 9183 mg/kg for SAPs. The PEC depended on the nature of the product, application rates and incorporation depth, as well as the soil bulk density. Available models have not been validated for polymers, thus, the derived PEC are to be used with caution. Given the persistence and low degradation of PAMs and PAAs in soil, soil organisms are expected to be exposed for a long time to such polymers, and accumulation in soil is therefore possible as well.

Ecotoxicological data of PAMs and PAAs were collected. The considered polymers have generally been thought to have low toxicity, because of their chemical inertness, their biodegradation and their large molecular size. Also the release of AMD is assumed to be negligible and commercial products must keep their monomer content under legal European limit values which do not exceed 0.1 % (e.g. European Commission 2002a, Italian Republic 2010, Anses 2012b). Scientific studies focused mainly on the effect of linear PAMs to aquatic organisms. Toxicity manifests as physical inhibition and depends on various parameters such as polymer charge, chemistry, species and is mitigated by suspended solids present in water. A Predicted No Effect Concentration (PNEC) of 0.05 mg/L for anionic linear PAM in water has been derived. Given their low potential of leaching and their sorption to solid particles, linear anionic PAMs might not cause a risk to aquatic, but could impact sediment dwelling organisms. On the other hand, degradation of PAMs and PAAs can lead to the formation of intermediate products, such as AA, which can be more mobile and toxic to aquatic life. Much less is known about the effects of linear PAMs to soil organisms and the few data indicated generally low toxicity. However, a PNEC of 0.5 mg/kg was derived and leads to a risk ratio greater than one for almost all the PECs considered. Finally, the small number of ecotoxicological bioassays on SAPs have indicated some adverse effects to plants or microorganisms at concentrations, which are much lower than the calculated PECs. However, these studies were not sufficient for deriving a PNEC.

Current regulations do not include a proper standardized risk assessment for polymers, and criteria for their registration and evaluation can vary depending on the country. Linear PAMs and cross-linked SAPs are commonly believed to have a low toxicity to the environment, but very few reliable ecotoxicological studies are available. Given their persistence, more bioassays on soil



organisms are required in order to better assess the risk for this compartment. In addition, the environmental degradation of PAMs/PAAAs needs to be investigated further, by means of field tests, aiming at evaluating the possible effect of intermediate products to soil and aquatic organisms. These conclusions are in line with the growing concern about the effect of polymers, as well as the need for a better knowledge about the impact of synthetic substances on soil organisms.



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1 Introduction

1.1 Context

Agriculture uses plant protection products and fertilizers including soil improvers that may contain various chemical substances. Among the latter, a growing sector is the application of polymers, such as polyacrylamide and polyacrylate, as improvers of the soil's water holding capacity (e.g. Mohana Raju, Padmanabha Raju, and Murali Mohan 2003, Abd El-Rehim, Hegazy, and Abd El-Mohdy 2004, Narjary et al. 2012, F. M. Chen 2016) or combined with fertilizers for a slow release of nutrients (e.g. Shavit, Reiss, and Shaviv 2003, Guo et al. 2005, R. Liang and Liu 2006a, Wu and Liu 2008, Tyliszczak et al. 2009, Rabat, Hashim, and Majid 2016, D. Liang et al. 2018). Acrylamide based co-polymers are also used as flocculants for the dehydration of gravel sludge and decarbonisation sludge, which are side-products of gravel and nuclear industry and that can be used as soil improvers. Also, digestates can contain residual polymer flocculants already present in the raw material. Acrylamide and acrylic acid – based polymers can then be applied to agricultural soils, either as a deliberate fertilizer component or indirectly as contaminants of fertilizers. The chemistry and the amount of polymers, which can be released, is variable.

To this point, no fertilizer containing polymers in order to increase soil water retention capacity has been authorized in Switzerland. Polymers used as coatings of fertilizers, in turn do not need an authorization as long as the coating substance is unhazardous for humans (DüBV 2013). Since ecotoxicological data for soil and aquatic organisms is scarce and limit values are missing, there is no consensus yet on how to quantify the risk for polymers. The use of digestates is authorised by the Federal Office of Agriculture (FOAG) if the product meets the criteria for being categorized under fertilizer type Nr. 2040 (DüBV 2013). Gravel sludges are provisionally authorised as mineral soil improvers until the end of 2020, while the evaluation process concerning a renewal of the authorizations for decarbonisation sludges is pending. Ecotoxicological data about flocculants, which are used for dewatering such substrates, is mostly limited to the aquatic compartment and little information is available for soil organisms.

In this context, FOAG has approached the Ecotox Centre to get support on the topic with the composition of a literature review summarizing the current state of the art on the ecotoxicological effects of polyacrylamide and polyacrylate on soil and aquatic organisms. Based on the data available, and when possible, provisional critical concentrations, where negative effects could be probable, were derived. In parallel, an evaluation of realistic exposure of the respective polymers in the environment was made in the context of the use considered in this study. A comparison between exposure and effect was finally discussed. This study aimed at summarizing the actual knowledge about soil and water ecotoxicological effects of polymers of use, as described above. Data gaps in the literature were reported and possible strategies for investigating further the effects of the chosen polymers were suggested. The information concerning polymers in digestates is provided in a separate document, because of the limited amount of data available.

1.2 Polymer definition and properties

In general terms, polymers are composed of a repeated chain of one same monomer (homopolymers) or of the alternation of many different monomers (co-polymers) (Deloitte 2014). According to their chemical composition, polymers can vary in chain length, molecular weight, structure, or charge, which makes each polymer unique and defined by specific properties. Given the high number of combinations possible, a huge number of different polymers exists and a clear definition on which classes need to be evaluated is necessary. This study focused on synthetic organic polymers, which contain acrylamide and/or acrylic acid.

Strictly speaking, polyacrylamides are defined as homo-polymers of only acrylamide (Green and Stott 1999). However, more commonly the literature classifies them in the broader group of products formed by the co-polymerization of acrylamide and other related co-monomers, which can have or not have further functionalization (Barvenik 1994). This latter definition will apply for



the rest of the report for polyacrylamides (PAMs). Depending on the nature of the composing monomers, hundreds of PAMs can exist, varying in chain length, number and types of functional groups substitutions, molecular conformation, or charge (Sojka et al. 2007). One main criterion commonly used for classing PAMs is charge density. Homo-polymers of acrylamide are by definition non-ionic, although they have actually a low degree of hydrolysis, which make them slightly anionic (Barvenik 1994). The co-polymerisation of acrylamide can provide a positive or negative charge to the PAM, depending on the nature of the co-monomers. Some common cationic co-monomers are diallyldimethylammonium, N,N,N-trimethyl-2-((1-oxo-2-propenyl)oxy) or 1,2-dimethyl-5-vinylpyridinium. Instead, PAMs become negatively charged, when hydrolysed or when co-polymerised with anionic co-monomers such as acrylate or 2-acrylamido-2-methylpropane sulfonate (Xiong et al. 2018). PAMs can be also distinguished by structure. Linear PAMs have a 2-dimensional chain configuration and are water soluble. The addition of cross-linking agents to the linear structure (e.g. N,N'-methylenebisacrylamide (BIS)) confers to PAMs a 3-dimensional network configuration, which is non soluble in water (Caulfield, Qiao, and Solomon 2002).

In a similar way, polymers can be composed by acrylic acid and other co-monomers. Care should be taken because definitions may vary depending on the publication. For instance, Ohara et al. (1950) define the polymers of acrylic acid and its sodium salt with the term poly(Acrylic Acid), and polymers composed by acrylic esters with the term polyacrylate. Nevertheless, many publications use the generic term “polyacrylate”, when referring to polymers composed by acrylic acid and related monomers, such as its salts (e.g. Mikkelsen 1994; Hüttermann, Oriquiriza, and Agaba 2009). As for PAMs, acrylic based co-polymers can also be defined by their structure, while charge is a less important factor in this context. In this study, only the cross-linked structure is considered, because it is the one used for agricultural purposes. To simplify, the acronym PAA will be used for the rest of this report, as a synonym of any polymer containing acrylic acid and/or related monomers (charged or not).

The polymers reviewed in the context of soil fertilization, as specified above, are either PAMs or PAAs. According to their main classification criteria (structure and charge) and to their use considered in this review, two main categories were defined (i.e. sections 1.2.1 and 1.2.2) and all the following analysis were done based on this distinction.

1.2.1 Linear PAMs (flocclulants)

Linear PAMs have a high versatility and have been widely used for a broad range of applications, the three largest uses being in wastewater treatment, paper and pulp processing and mineral processing (European Commission 2002a). High molecular weight PAMs (10^6 to 10^7 gmol⁻¹) are mainly used as flocculants/coagulants for facilitating the solid-phase separation of various sludges or contaminated waters/effluents (Guezennec et al. 2015). Both cationic and anionic PAMs can be used, the first are primary used as coagulant (via electrostatic attraction to particles), while the latter are mainly used as flocculants, by bridging the primary flocs into bigger aggregates (Letterman and Pero 1990; Mortimer 1991). Non-ionic PAMs also have been reported to be applied, mainly as flocculant aids of primary coagulants, in the context of water clarification and mineral processing (Barvenik 1994). However, the use of ionic PAM was indicated to be more widespread than non-ionic, already in the early 90s (Mortimer 1991). Anionic PAM flocculants have been reported to be widely used for the dewatering of sewage sludge, and in various other domains like mining, paper manufacture, clarification of refined sugar and fruit juices (Entry et al. 2002). Other important applications of anionic linear PAMs are also reduction of construction-related suspended sediments and turbidity (Buczek et al. 2017), as well as erosion control and soil stabilization in agriculture and land management (Sojka et al. 2007). In the context of the present study, the targeted polymers are PAM flocculants used for sludge dewatering. Linear PAMs are added at the end of the treatment to these substrates, in order to aggregate solid particles and to facilitate the extraction of the solid phase. The resulting product is then a mostly solid sludge, containing residual PAM flocculants as contaminants. PAMs used for such



applications seem to be generally anionic. However, material safety data sheets are often not publicly available from manufacturers. A few examples of PAM flocculants have been provided from FOAG, which were all anionic. These products were used for the derivation of a realistic exposure scenario (see section 2.2.1). Detailed information on the specific products was omitted in this report though for confidentiality reasons. The names of the specific products were anonymized by using letters instead of the real product names. The product names and characteristics are provided in a separate confidential document available only to the FOAG. In this report, it was assumed that, given the anionic character of the product cases considered, other polymers having the same use would also be anionic. However, their charge density should preferably be checked for each specific formulation.

1.2.2 Cross-linked SAPs (hydrogels)

Cross-linked polymers are synthesized specifically for their ability to absorb large amounts of water in their network (Demitri et al. 2008). They generally have a high molecular weight as well, ranging from 10^3 to 10^6 g/mol (Parks 1981). Their common cross-linked structure allows them to store water because of their hydrophilic character and to swell until reaching several hundred times their initial weight (Wolter et al. 2002; M. O. Ekebafé, Ekebafé, and Maliki 2013). For this reason, they are included into the wider group of superabsorbent polymers (SAP) or hydrogels. SAPs have been used for various applications, such as ingredients in hygiene articles with high liquid holding capacity (e.g. baby diapers, sanitary napkins, incontinence products) or for packaging of food products to lengthen shelf life (Sutherland, Haselbach, and Aust 1997; Mai et al. 2004; F. M. Chen 2016). Other uses are for biomedicine production, drug delivery systems and contact lenses production (Mohammed and Kmal 2012). Another important application, and the one analysed in this report, is their use for horticulture for improving soil water holding capacity, found to be efficient especially in arid areas, by acting as “water-reservoir” when the water is limited (Zohuriaan-mehr and Kabiri 2008). SAPs have been thus demonstrated to enhance the availability of water and reduce water stress to plants (Holliman et al. 2005; Hüttermann, Oriquiriza, and Agaba 2009). Another use of SAP is in combination with fertilizers (e.g. coatings): by holding the nutrients and delaying their dissolution, hydrogels limit the loss of nutrients into the environment and increase the availability of nutrients for plants (Zohuriaan-mehr and Kabiri 2008; Shen, Du, and Zhou 2014). Slow release of nutrient and moisture preservation, can also be applied together (e.g. Guo et al. 2005). Cross-linked hydrogels have been proven in several cases to promote plant growth (Mohammed and Kmal 2012). Most common synthetic hydrogels are cross-linked PAMs and PAAs. In general, acrylic acid is combined with either acrylamide or one of its salts, forming sodium or potassium polyacrylate (Na or K-PAA) (L. O. Ekebafé, Ogbeifun, and Okieimen 1984; Hüttermann, Oriquiriza, and Agaba 2009). Several hydrogel products (both “pure” hydrogels and hydrogels combined with fertilizers) were evaluated in this report as examples for deriving a realistic exposure scenario (see section 2.2.2). Such products were all composed of either K PAA or K PAM. As for linear PAMs, detailed information about the manufacturers and technical characteristics of the products are only provided separately, in a confidential document for the FOAG and the product names are anonymized by using letters here.

The European Commission provides a database for the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), in order to avoid possible risks to humans and to the environment (ECHA 2019). However, polymers cannot be defined by a unique specific chemical formulation, since combination of their composing monomers is almost limitless, and their composition is variable. Polymers are thus not included in the REACH provisions, set out in the title II (Registration) and title VI (Evaluation) (REACH 2006). As a consequence, many PAMs and PAAs are not included in chemical databases. Some simple polymers are registered under a CAS number, such as Poly(acrylic acid) homo-polymer – CAS n. 9003-01-4, Polyacrylamide homo-polymer, CAS n. 9003-05-8, Acrylamide/sodium acrylate copolymer n. 25085-02-3, or Poly(acrylamide-co-acrylic acid) potassium salt, CAS n. 31212-13-2. However, these polymers are either not representative of the ones used in fertilizing practices (e.g. homo-polymers) or they



do not belong to a harmonized classification, and their potential hazard is not evaluated (ECHA-Substance Information, 2019). On the other hand, their composing monomers are registered and their impact on the environment is relatively well known. The following section (1.3) summarizes the characteristics of such monomers, including their environmental behaviour and hazard statements. The rest of the report focused on the two categories of polymers of interest for this study. Following an approach, similar as for the Risk Assessment Evaluation method commonly used for chemicals (e.g. REACH), the chapter 2 provides information on environmental exposure of the polymers, including their environmental behaviour (degradation, stability, sorption,...) as well as an approximation of realistic environmental exposure scenarios. The following chapter (3) focused on the effect assessment, based on ecotoxicological data found in the literature and derived, where possible, Predicted No Effect Concentrations (PNECs). Finally, the comparison between realistic exposure and potential effect was made (chapter 4), in order to discuss the safety of the use of these substances. A comparison with approaches and regulations used in some other countries was also done.

1.3 Monomers definition and properties

In this section, only properties and hazards are presented, which can be directly related to their use as considered in this report. The focus was on the behaviour and on the impact of the monomers on especially the soil and the water compartment. Additional information, such as human toxicity or releases and risks evaluated, based on uses other than the ones considered here, were therefore mostly omitted.

1.3.1 Acrylic acid (AA)

1.3.1.1 Identification and properties

Main properties and identification of AA are defined in the Table 1.

Table 1: Some general information about acrylic acid

Characteristic / property	Value	Reference
CAS-No.	79-10-7	
IUPAC name	2-propenoic acid	
Molecular weight	72.06 g·mol ⁻¹	
Molecular formula	C ₃ H ₄ O ₂	European Commission 2004b
Structural formula	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{OH} \\ \\ \text{H}_2\text{C} = \text{C} - \text{H} \end{array} $	
Physical state	liquid at 20°C and 1013 hPa	
Octanol – water partition Coefficient (log Pow)	0.46 at 25°C	ECHA-Dossier 15803, 2019
Water solubility	1000 g/l at 25° C	
Dissociation constant (pKa)	4.26 at 25° C	

The European Commission provided a detailed Risk Assessment for the substance Acrylic acid (AA) in 2002. If not differently specified, the following statements were derived from the Summary of their Risk Assessment Dossier (European Commission 2002c).



1.3.1.2 Environmental behaviour

AA has been shown to be readily biodegradable under environmental conditions. No relevant adsorption to sediment or soil is indicated. AA is highly mobile within the soil. According to the models reported in the European dossier, more than 99 % of total AA is expected to be found in the water compartment, where it is highly soluble. Neither relevant bioaccumulation nor geoaccumulation was indicated.

1.3.1.3 Effect assessment

A PNEC has been derived for water, basing on the lowest valid effect concentration (30 µg/l in an algae test). Using an assessment factor of 10, the PNEC_{aquatic} has been calculated to be equal to 3 µg/l. Given no relevant adsorption to soil particles, the PNEC for sediment has not been performed. For soil, only one test on respiration inhibition was available, leading to a PNEC_{soil} of 0.1 mg/kg. The PNEC_{aquatic} of 3 µg/l can also be used and suggested to be compared to the concentration in soil pore water, for assessing the risk for the soil compartment.

1.3.1.4 Environmental classification/hazard statements

Classification and labelling, according to the 28th ATP of Directive 67/548/EEC (European Commission 2001) are the following:

R10 Flammable
 Xn; R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
 C; R35 Corrosive; Causes severe burns
 N; R50 Dangerous for the environment; very toxic to aquatic organisms
 C; N
 R: 10-20/21/22-35-50
 S: (1/2-)26-36/37/39-45-61

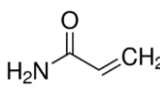
Focusing only to the environmental concern, AA presents a very high toxicity for aquatic life, according to the harmonized classification and labelling (CLP00) approved by the European Union (ECHA – Substance Information, 2019).

1.3.2 Acrylamide (AMD)

1.3.2.1 Identification and properties

Main properties and identification of AMD are defined in the Table 2.

Table 2: Some general information about acrylamide

Characteristic/property	Value	Reference
CAS-No.	79-06-1	
IUPAC name	acrylamide	European Commission 2002a
Molecular weight	71.09 g·mol ⁻¹	
Molecular formula	C ₃ H ₅ NO	
Structural formula		Sigma Aldrich, 2019
Physical state	odourless, white, crystalline solid at 20°C and 1013 hPa	
Octanol – water partition Coefficient (log Pow)	-0.9 at 20°C (very low)	ECHA-Dossier 15534, 2019
Water solubility	2,155 g/L at 30°C	
Dissociation constant (pKa)	not applicable/not available	



Similarly as for AA, the risk of Acrylamide (AMD) has been assessed by the European Commission in 2004 (European Commission 2002a). If not differently specified, the following statements are derived from the conclusions of their Risk Assessment Dossier.

1.3.2.2 Environmental behaviour

AMD has been indicated to be relatively mobile in most soil types, and adsorption is very low. In addition, it is highly soluble in water. Transfer models reported in the risk assessment dossiers, indicate that water is the most important compartment for acrylamide. The potential for bioaccumulation is indicated as low. In addition, when PAMs are applied to crops, the uptake of AMD from plants is generally very low (Castle 1993; Bologna et al. 1999).

AMD is readily biodegradable. Lande, Bosch, and Howard (1979) reported that, following a PAM application of 25 kg/kg to the soil, AMD was rapidly biodegraded within a few days (18–45 h) to CO₂, NH₄ and H₂O, with formation of AA as intermediate, which is as well readily biodegradable and mobile in the soil. Also AMD was completely degraded within 5 days after applying 500 kg PAM/kg garden soil (Shanker, Ramakrishna, and Seth 1990).

1.3.2.3 Effect assessment

Based upon all of the available data, the EU derived a PNEC_{aquatic} of 20.4 µg/l. A slight toxic effect on plant growth, and no effect on seed germination were reported at a concentration of 10 mg AMD/kg soil. Other results were limited and did not allow a PEC calculation for the soil. The PNEC_{aquatic} of 20 µg/l for the aquatic compartment is then suggested to be used for risk assessment. Finally, AMD was indicated as not accumulative or persistent in the environment.

1.3.2.4 Environmental classification/hazard statements

Classification and labelling, according to the 28th ATP of Directive 67/548/EEC (European Commission 2001) are the following:

Carc.Cat. 2; R45	May cause cancer
Muta.Cat. 2; R46	May cause heritable genetic damage
Repr.Cat. 3; R62	Possible risk of impaired fertility
T; R25-48/23/24/25	Also toxic: danger of serious damages to health by prolonged exposure through inhalation, in contact with skin and if swallowed
Xn; R20/21	Also harmful by inhalation and in contact with skin
Xi; R36/38	Also irritating to eyes and skin
R43	May cause sensitization by skin contact

No classification for the environment.

According to the **harmonised classification and labelling** (CLP00) approved by the European Union, this substance is toxic for humans and animals and is of very high concern. However, no classification is available for the environment.

PAMs might contain some residual levels of AMD monomers, originating from the production. Given its high toxicity, the residual content of acrylamide in the polymers is kept below 0.1 % w/w to avoid classification as a Category 2 carcinogen under the Dangerous Preparations Directive (88/379/EEC and adaptations). (European Commission 2002a).



2 Environmental exposure

Environmental exposure was assessed through two steps. First, a description of the environmental behaviour and fate of the concerned polymers based on available literature was provided. Behaviour such as degradation, stability, sorption, mobility and bioaccumulation was evaluated in order to identify in which environmental compartments polymers are likely to be released and transferred to. Secondly, an exposure scenario for each use was investigated in detail, based on available information about their release amount to the environment, a prediction of concentrations of polymers, which can be found in the environment was derived for each situation.

In the context of this study, PAMs and PAAs can be released into the environment through two main ways. In the first, linear PAMs can be found as contaminants from the production of some soil improvers, such as gravel sludge and decarbonisation sludge. Following their application, residual PAMs can thus enter in the soil compartment. The second scenario is the direct application into soil of cross-linked SAPs as proper soil conditioners as water retention improvers, or as fertilizer coatings. The two categories of polymers and their consequent possible exposure were treated separately in the two following sections.

2.1 Environmental fate

2.1.1 Stability and degradation

Detailed information available from the literature is large concerning the degradation mechanisms of PAM (linear and cross-linked), while studies on acrylate-based SAPs are mainly based on their biodegradation. For this reason, this chapter is structured presenting first degradation pathways for all PAM structures and secondly presenting additional information on biodegradation for PAAs, concluding with their environmental stability. The information presented in this section are summarized in the Table 3.

2.1.1.1 PAMs (linear and cross-linked)

Degradation mechanisms of both linear and cross-linked PAMs have been reviewed and investigated by Caulfield et al. (2002, 2003a, 2003b) and most recently summarized by Xiong et al. (2018). Sojka et al. (2007) also reported information of PAM degradation in their review focusing on linear anionic PAMs used for soil erosion control. Based on the study of Azzam (1983) which analysed the efficacy of a cross-linked PAM gel mixed into the soil, Sojka and co-workers applied their conclusions also for linear PAM, stating that degradation under environmental conditions can occur, as a result of chemical, photochemical, mechanical or biological processes. The major degradation paths which are likely to occur under environmental conditions are briefly summarized here. Thermal degradation is not reported because it is not likely to occur under 200°C (Caulfield, Qiao, and Solomon 2002). However, high temperatures can increase both chemical and photolytic degradations (Xiong et al. 2018).

Chemical degradation of PAMs concerns mostly hydrolysis of the amide group and involves often the action of free radicals, which in turn leads to subsequent chemical reactions (e.g. hydroxyl, potassium persulfate $K_2S_2O_8$ or hydrogen peroxide H_2O_2). This is generally faster for linear PAMs than cross-linked PAMs (Caulfield, Qiao, and Solomon 2002). In addition, Xiong et al. (2018) reported the important role of dissolved oxygen and Fe^{2+} in increasing the chemical degradation of PAMs under environmental conditions.

Photolytic degradation is also induced by free radicals, which are released when photons have sufficient energy to break the chemical bonds of the polymer (Caulfield, Qiao, and Solomon 2002; Xiong et al. 2018). UV rays have higher energy and are believed to have a stronger influence than visible light. As the most energetic part of the UV spectrum is absorbed by the atmosphere, the remaining part which reaches the soil can only break the C-C bond, but has minimal impact



on stronger bonds such as C-H or C-N (Smith, Prues, and Oehme 1997). The presence of oxygen can easily increase the degradation process, leading to a series of complex photooxidations and causing irreversible changes in properties of the polymer (Caulfield, Qiao, and Solomon 2002). Photodegradation is expected to play a major role when PAMs are applied combined with irrigation, because of longer exposure to sunlight, while its effect is reduced when they are directly mixed with the soil (Sojka et al. 2007; Xiong et al. 2018). The depolymerization of PAM into AMD under photolytic degradation has been questioned and will be discussed in the section 2.1.1.3.

Mechanical degradation is caused by external mechanical stimuli, which can alter both aqueous or liquid polymer phases (Caulfield, Qiao, and Solomon 2002). Similarly to photolytic degradation, sufficiently high mechanical energy can break chemical bonds by liberating free radicals. Physical properties (e.g. viscosity) are generally irreversibly altered (Caulfield, Qiao, and Solomon 2002). Mechanically induced degradation is believed to occur mostly during industrial applications of aqueous PAM solutions, such as oil and gas processing (Xiong et al. 2018), but it can happen also in the soil under environmental conditions, for instance by tillage abrasion or freezing and thawing (Sojka et al. 2007).

Compared to the other processes, literature about **biodegradation** of PAM is more limited. Under biodegradation, changes in the structure of the polymers take place (Caulfield, Qiao, and Solomon 2002). Microbial degradation depends on the nature of the polymer (Caulfield, Qiao, and Solomon 2002) and on the microflora present in the soil (Hüttermann, Orikiriza, and Agaba 2009; Sanz Gómez et al. 2015). Given their high molecular weight, PAMs are too large to penetrate biological membranes and only certain microorganisms having specific enzymes (e.g. extracellular), are able to degrade them (Caulfield, Qiao, and Solomon 2002). In the literature, different varieties of microorganisms have been demonstrated to degrade PAM under experimental conditions. Some bacterial strains were found to be able to utilize linear PAM as sole source of nitrogen (Kay-Shoemake et al. 1998). There is less evidence of use as source of carbon, but when this occurs (e.g. Nakamiya and Kinoshita 1995), this is believed to be in combination with abiotic processes which break them firstly into smaller fragments, favouring the absorption by microorganisms (Caulfield, Qiao, and Solomon 2002). An enzyme effective in PAM biodegradation is the lignin degrading enzyme (Caulfield, Qiao, and Solomon 2002). Under favourable conditions, white rot fungi was found to depolymerize efficiently both cross-linked and linear PAMs (Stahl et al. 2000; Mai et al. 2004). Solubilisation and mineralization of cross-linked co-polymers of AMD and AA were reported to be much more rapid than these of cross-linked PAAs without AMD comonomers (Stahl et al. 2000). Holliman et al. (2005) reported that linear PAMs seem much easier attacked by soil amidases. Wolter et al. (2002) measured a rate of mineralization of 9 % of the initial radioactivity of a ^{14}C labelled cross-linked PAM, after 22 weeks, in a soil that was inoculated the white rot fungus *Pleurotus ostreatus*. However, without addition of fungal substrate, mineralization rate was only 2.2 %. Although some PAM-degrading microorganisms can be naturally found in soil, sludge or waste water (Xiong et al. 2018), it should be noted that most of the reported studies were based on experimental microcosms, with inoculation of specifically selected microorganisms and/or under favourable conditions, hence not necessarily reflecting realistic environmental conditions.

Under **environmental conditions**, linear PAMs were reported to be generally stable by Seybold (1994), because of their low microbial degradation. The authors suggested that physical changes can most likely be attributable to environmental factors, such as sunlight, chemical hydrolysis, and mechanical degradation. Azzam (1983) estimated a global degradation rate of approximately 10 % per year for cross-linked PAM gels, incorporated to soil, through abiotic and biotic processes. This value has been reported by main publications, and assumed to be valid for both linear and cross-linked PAMs (e.g. Wallace and Wallace 1986; Sojka et al. 2007; Young et al. 2007; Paz-Alberto et al. 2011). Holliman et al. (2005) also concluded that cross-linked PAMs might last several years in the soil until complete biodegradation, based on the very slow biodegradation rate observed in their experiments, even in enriched bacterial cultures. Hennecke et al. (2018) calculated a mineralization rate of a linear PAM of 22.5 % within a period of 2 years in the soil, based on a conservative approach. Both linear and cross-linked PAM are then



relatively resistant to microbial attack under environmental conditions (Caulfield, Qiao, and Solomon 2002; Yu et al. 2011).

Finally, given their solubility, linear PAMs can potentially reach the water compartment. Degradation was reported to be much faster in aqueous solutions than in soil. For instance, more than 70 % of a PAM flocculant was degraded after 96h in aqueous solution with two bacterial strains (Feng et al. 2009). The difference between soil and water is surely due to polymer adsorption to soil particles which make it less available for microorganisms (Anses 2012c).

2.1.1.2 PAAs (cross-linked)

Literature about degradation of PAA is mostly focused on their microbial degradation, and tends often to consider together the wider group of SAPs, which can contain or not also AMD. Most of the considerations made for cross-linked PAMs are then applied also for PAA gels, and this section will thus only report specific considerations made for PAA or summarize the conclusion made on PAM gels.

As for PAMs, thermal degradation is unlikely to occur for PAA if not at high temperatures (400°C) (McNeill and Sadeghi 1990). Degradation mechanisms under environmental conditions are expected to be mostly driven by mechanical, chemical and biological processes, in a similar way than described for PAMs.

As for PAMs, also cross-linked PAAs generally need to be broken into smaller fragments by abiotic mechanisms first in order to be absorbed by microorganisms for further degradation (Hayashi et al. 1994). Some selected microorganisms have also been reported to effectively degrade cross-linked PAAs under favourable conditions, even if at lower rates than PAMs (Sutherland, Haselbach, and Aust 1997; Stahl et al. 2000; Mai et al. 2004). Some bacteria were found to degrade efficiently PAAs, in a similar way than the metabolism linked to respiratory chains (Kawai 2007). The degradation rate of acrylate based hydrogels in compost was 5.9 % under aerobic conditions after about 500 days (Stegmann et al. 1993). Wilske et al. (2014) found a mineralization rate of 0.12–0.24 % on 6 months for PAA SAP in agricultural soil, confirming their slow degradability under common environmental conditions. A weight loss of 1.77 % after 12 months was observed by D. Liang et al. (2018) for a PAA fertilizer coating in agricultural field soil. Similarly, the degradation of another PAA waterborne coating resulted in a weight loss of 1.69 % after 12 months, when buried in the soil of a wheat field (Dong et al. 2019).

Hüttermann and co-workers (2009) reported biodegradation of PAA to range from 1-9 % per year, similarly to the one of PAMs. The authors stated that such decomposition rate was comparable to that of natural organic matter in forest ecosystems. Since this is comparable to natural humus cycles, SAPs (both AMD- and AA-based) have often been seen like “artificial humus” and considered to be eco-compatible and thus non-toxic (Hüttermann, Orikiriza, and Agaba 2009; Sanz Gómez et al. 2015).

2.1.1.3 Degradation products

PAM/PAA degradation can lead to the formation of new molecules, which can have different properties from the original polymer. For instance, their lower molecular weight can lead to higher mobility, or hydrolysis can make these by-products more hydrophilic, due to the higher number of carboxylic groups. For this reason, it is important to investigate the release of by-products and consider their potential environmental impact (Xiong et al. 2018). Some common groups formed by chemical, photolytic and thermal decomposition of PAM are ketones, aldehydes, and carboxylic groups while no information has been found for mechanical degradation (Xiong et al. 2018). Under complete degradation PAM is expected to be transformed into carbon dioxide and ammonia/nitrogen (Smith and Oehme 1991; Caulfield, Qiao, and Solomon 2002). At high temperatures, formation of intermediate products, among which AA, has been reported as well (Bologna et al. 1999; Caulfield, Qiao, and Solomon 2002). A recent French report highlighted the possibility that linear PAM introduced into the soil could degrade into PAA, leading to AA releases, which in turn could leach into ground waters (Anses 2012a). Also, under anaerobic conditions,



important amounts of AMD, AA and PAA were observed as intermediate products from degradation of linear PAM (D. Wang et al. 2018). Degradation of PAAs can also lead to a wide range of dimer and trimer fragments (McNeill and Sadeghi 1990). PAA hydrogels contain already amounts of residual AA, which are neutralized by combining the polymer with sodium or potassium hydroxide during their production (Mohammad J. Zohuriaan-Mehr and Kabiri 2008). However, the final SAP product can still contain some high amounts of free AA (X. Chen et al. 2016). Concerning biodegradation, the monomers and dimers produced by both linear and cross-linked, PAAs and PAMs were generally found to be non-toxic for degrading microorganisms and readily mineralized by microflora (Larson et al. 1997; Sutherland, Haselbach, and Aust 1997).

The main concern about degradation of PAM has been the possible formation of AMD monomers, which is a common carcinogenic and neurotoxic. AMD residues are already present in commercial products and their content is kept below legal limits (see 1.3.2). AMD is believed not to be released through mechanical, chemical or aerobic biological processes but some concerns have been risen concerning photolytic and thermal effects (Caulfield, Qiao, and Solomon 2002; Holliman et al. 2005; Xiong et al. 2018). The degradation of a linear PAM was first investigated by Smith et al. under artificial and outdoor conditions in aqueous solutions (1996, 1997). The authors detected levels of AMD monomers at both conditions, suggesting that PAM is not stable in the environment and that it could be depolymerized into monomers under photolytic (UV) and thermal effects. They also observed that AMD was already present as residual monomer in the studied PAM. In parallel, they did not observe the presence of AMD in the run-off water when PAM was incorporated to the soil, suggesting that the adsorption to soil particles limited PAM degradation or that PAM was degraded into other by-products than AMD. However, the reliability of their results has been questioned by many other researchers, suggesting mostly that the polymer purification and characterization methods used by Smith and co-workers were not optimal and that this could have led to misleading conclusions (Caulfield, Qiao, and Solomon 2002). For instance, Ver Vers (1999) repeated the study on degradation of PAM under conditions similar to Smith's, but did not detect any release of AMD. They concluded that photolytic degradation does not lead to AMD formation and contested the efficiency of the method used by Smith for analysing AMD levels. This was consistent with studies of Kay-Shoemaker et al. (1998) and Gao et al. (1998), who did not detect any release of AMD from soluble PAMs exposed to UV irradiation and at low temperatures neither. A parallel study revealed no considerable accumulation of AMD in crops treated with linear PAM, and concluded that AMD was unlikely to be released under environmental conditions (Bologna et al. 1999). The same authors questioned the results of Smith et al. (1996, 1997), suggesting that if depolymerized had actually occurred, then the amount of AMD released would have been much higher than the one observed. Caulfield et al. (2002) concluded from the literature data, that the starting material polymer used by Smith and co-workers (1996, 1997) was impure and contained probably already detectable residues of AMD, coming from the manufacturing.

Given these controversial results available, Caulfield et al. investigated successively the degradation of both linear and cross-linked PAM under laboratory conditions. They demonstrated that, in aqueous solution, linear PAM was stable under room temperature and thermal irradiation (95°C) with no release of monomers or other toxic compounds. Under UV irradiation, only very small levels of AMD (<50 ppm) were detected and were supposed to be due to chain scission, not an unzipping of the polymer chain (Caulfield, Qiao, and Solomon 2002). Cross-linked PAMs were also stable at room temperature but a release of AMD was reported at 95°C and might be due to the pendant unsaturation of the cross-linking agents. Irradiation of UV induced as well a low release of AMD (1 molecule of AMD / 2000 monomer units) (Caulfield et al. 2003). These results suggest that, under environmental conditions, AMD release should not occur from degradation of linear PAM, while cross-linked PAM have the potential of AMD release under high temperatures. Holliman et al. (2005) further investigated the environmental degradation of cross-linked PAM gels, by incubating new and field-conditioned gels, used during the revegetation of slate waste during a period up to six years. While freeze-thaw cycles and UV irradiation had no influence on AMD formation, the authors detected the presence of AMD in all observed gels. In



new manufactured gels, AMD levels exceeded EU legal limits for drinking waters (0.1 ug/l), after 22 weeks of incubation at both 20 °C and 35 °C. However, these levels were below legal limits of 0.25 g/kg, fixed for commercial manufactured PAM products in Europe for all new and field-conditioned gels incubated at 20 °C. Legal limits were exceeded only for field conditioned gels incubated at 35 °C. Similar trends were observed for AA release. They concluded that PAM gels are relatively stable under field conditions, producing low levels of AMD, which in turn degrades very quickly in soil. However, a higher formation of AMD was demonstrated to occur at 35 °C, suggesting that PAM may be unsuitable for warm climates.

2.1.1.4 Conclusion and environmental concern

Degradation of PAMs and PAAs under environmental conditions in the soil is expected to be influenced by temperature, sunlight, pH, humidity and salt content, and is subjected to seasonal variations (Sojka et al. 2007; Barvenik 1994; D. Liang et al. 2018). In soil, the main processes are believed to be mechanical, chemical and biological (Barvenik 1994; Holliman et al. 2005). Both PAMs and PAAs are relatively resistant to microbial attack under environmental conditions, and have a low degradability in soil, with rates expected to be not more than 10 % per year and depending on their structure and composition. Linear PAMs seems to degrade faster than cross-linked PAMs, while cross-linked PAAs seem even more resistant. According to the REACH Regulation this would be enough to characterize all PAM/PAA polymers as persistent substances (ECHA 2017). In addition, the rate exceeds largely the trigger values proposed by the European Union for persistent chemicals, below which an ecotoxicity test with terrestrial species would be required (EU 2002).

There is a general agreement that PAM do not release AMD under mechanical, chemical or biological degradation (Caulfield, Qiao, and Solomon 2002). However, the release through photolysis is still questioned. In addition, cross-linked gels have been shown to form AMD under high temperatures in the soil. For both PAM and PAA, data about degradation are mainly based on controlled laboratory conditions, which might not reflect adequately field conditions. For these reasons, the behaviour of PAMs and PAAs in the field still need to be elucidated, in particularly regarding their fate, long term degradation in the soil and the formation of by-products, not only AMD but also AA and others (Anses 2012a; Sanz Gómez et al. 2015; Xiong et al. 2018).

SAPs are used for a wide range of other industrial products (see 1.2.2). When focusing mostly on other uses than agriculture, a growing concern is observed in the literature about cross-linked PAM and PAA gels, which are considered to have a slow biodegradability and possible toxic effects to the environment. Therefore more natural alternatives, especially polysaccharides, are now receiving more attention, because are considered more eco-compatible than synthetic polymers (Esposito et al. 1996; Al et al. 2008; Fajardo et al. 2015; Zhou et al. 2015). Natural polymers such as pectin, cashew gum, Arabic gum, starch, chitosan, chitin, cellulose or lignin are largely studied, both as substitute or as combination with synthetic polymers (grafting), in order to improve their biodegradation in the context of various application, including also agriculture (Mai et al. 2004; Fajardo et al. 2015). Environmental concern has risen as well for synthetic polymers used as flocculants, because of their low biodegradability and the presence of carcinogenic monomers (Shih et al. 2001; Shirzad-Semzar, Scholz, and Kulicke 2007; You et al. 2009). Similarly to cross-linked gels, substitutes to linear synthetic polymers are being evaluated, based on renewable primary products (e.g. cationic starches chitosan, polysaccharides) (Roussy, Van Vooren, and Guibal 2004; Shirzad-Semzar, Kulicke, and Lotz 2007). Some starches are already used with success and proven to be less toxic (e.g. Krentz et al. 2006). In this context, Germany aimed to gradually replace synthetic flocculants with cationic starches (Shirzad-Semzar, Scholz, and Kulicke 2007).

2.1.2 Sorption

Linear PAM have generally a strong affinity to soil particles, with degree of adsorption depending on PAM conformation and soil characteristics (Sojka et al. 2007). Generally, adsorption is



increased by increasing molecular weight and chain extension (Malik and Letey 1991). Cationic are more strongly adsorbed to soil (electrostatic interaction with negative particle charge), followed by non-ionic (Van de Waals) and by anionic (cationic bridges) (Seybold 1994). Clay and organic matter present in the soil also increase the adsorption (Biesinger et al. 1976; Goodrich et al. 1991; Hall and Miranda 1991). Adsorption is mostly irreversible and once they are bound, polymers are very difficult to desorb, which results in a very low mobility (Nadler, Malik, and Letey 1992; Sojka et al. 2007). SAPs are also reported to strongly adhere to soil particles, and eventually become components of the soil (R. Liang and Liu 2006b). However, mobility by run-off could be expected if polymers are bound to sediments.

2.1.3 Bioavailability and bioaccumulation

Bioavailability is strongly reduced in aqueous solution when PAM are bound to suspended particles (Buczek et al. 2017). Given their large molecular size, PAM is not able to penetrate biological membranes and have been reported to have low risk of bioaccumulation (NICNAS 2002; Stephens 1991). This consideration is likely to be valid also for cross-linked PAAs, because they have as well a high molecular weight. However, little is known on the behaviour of smaller fragments, formed by degradation of PAM (Xiong et al. 2018).

2.1.4 Environmental distribution

Once applied to the field, PAMs and PAAs are likely to bind strongly to soil particles. Given their high molecular weight and low potential for desorption, translocation is then little probable and PAMs are expected to remain for a long time in the soil compartment, where degradation has been shown to be slow (Smith and Oehme 1991; Xiong et al. 2018). For these reasons, they have a potential to accumulate in soils, which are treated with these polymers (Orts, Sojka, and Glenn 2000; Anses 2012c; Watson et al. 2016). Transfer to water is expected to be very low. Weston, showed that linear PAM, applied as sprinkler irrigation, adsorbed partially to the soil, but approximately half of the original concentration remained in the tail water. However, if PAMs/PAAs are applied as a solid form and are directly mixed with soil, leaching should be reduced. Malik and Letey (1991) found that PAM remained at the same depth, where it had been applied even 10 months after application with furrow irrigation and with 720 mm of additional water application. Sojka, Entry, and Fuhrmann (2006) reported that, given their high sorption and low mobility, linear PAMs do not move more than a few centimetres from its point of entry into the soil. Hennecke et al. (2018) confirmed that PAM contained in a sludge applied to a field, was mostly immobile in soil as only 6.5 % was translocated beyond the top 10 cm. This minor part was more likely moved by mechanical movement due to sowing and harvesting. However, given their strong adsorption to soil particles, polymer transfer to sediments cannot be excluded (Weston et al. 2009).

AMD is unlikely to be released under environmental conditions. Lentz et al. (2008) have confirmed that AMD is not released into ground waters, following linear PAM application to soil for erosion control. If present, it has low probability of accumulation or transfer to ground waters due to its rapid biodegradability in the soil.



Table 3: Summary of the environmental fate of PAMs and PAAs. Only the processes occurring under environmental conditions are taken into account. NA indicates processes for those not enough information was available. For PAM products, the possibility of AMD release is indicated as well

Process	PAM		PAA
	Linear	Cross-linked	Cross-linked
Degradation in the soil	Thermal	Not likely (>200°C) but high temperatures can increase chemical and photolytic processes. AMD release not likely	Not likely (>200°C) but high temperatures can increase chemical and photolytic processes
	Chemical	Promoted by free radicals, such as Fe ²⁺ and O ₂ . Faster than cross-linked. AMD release not likely	Promoted by free radicals, such as Fe ²⁺ and O ₂ . Slower than linear. AMD release not likely
	Mechanical	Involves free radicals, likely only in case of tillage and abrasion. AMD release not likely	
	Photolytic	Involves free radicals, C-C bond scission, photooxidation reactions in presence of oxygen. This degradation way is less likely when the polymer is mixed into the soil. AMD release debated	
	Biodegradation	Needs specific microorganisms and enzymes. Mostly in combination with abiotic factors (break into smaller fragments). Rates are generally not more than 10 % per year. AMD release not likely	
Degradation in the water	Much faster than in soil, because of less sorption to solid particles		
Persistence in the soil	Can be considered as persistent		
Sorption to soil particles	Strong and mostly irreversible		
Bioavailability/bioaccumulation	Low because of soil sorption and high molecular weight		
Environmental distribution	Low mobility and high persistence in the soil lead to high potential of accumulation in the soil. Transfer to water likely through sediment run-off		

2.2 Environmental release

Since they are not covered by the common regulations for risk assessment, such as REACH regulation, validated models predicting environmental exposure for regulatory purposes are not available. Two models are commonly used for assessing the Predicted Environmental Concentration (PEC), based on the guidelines proposed by the FORum for the Co-ordination of pesticide fate models and their Use (FOCUS) and by the European Medicines Agency (EMA), respectively. However, these two models are specifically conceived for organic pesticides (FOCUS) or pharmaceuticals (EMA) and they have not been validated for polymers. The results obtained from these models are thus to be considered as an approximation, to give an idea of potential realistic concentrations, but they cannot be used for a proper risk assessment. Specific models evaluating the environmental fate of PAMs and PAAs are required. A distinction should also be made between linear and cross-linked polymers, as their potential of leaching with waters will be different depending on their water solubility.



For each category, the method for evaluating the exposure assessment included the following steps:

1. Estimation of flocculant concentration

Valid for sludges: based on existing information, the amount of flocculant, which is likely to be present in the substrate is derived.

2. Application rates

A collection of available application rates and recommendations was considered, and the lowest and the highest dose were taken as a best- and worst-case, respectively. Where specified, the depth of incorporation into the soil was taken into account. Otherwise, default values reflecting incorporation and no incorporation were used (see above).

3. PEC derivation

The first step of the final report of the Soil Modelling Work group of FOCUS (FOCUS 1997) allows the calculation of the initial PEC of a pesticide in the soil, immediately following a single application, according to the Equation 1:

$$\text{Initial PEC}_s = \frac{A \times (1 - f_{\text{int}})}{100 \times \text{depth} \times \text{bd}}$$

Equation 1

The parameters are the following:

- Initial PEC_s = Predicted Environmental Concentration in soil after a single application [$\text{mg} \cdot \text{kg}^{-1}$]
- A = Application rate [$\text{g} \cdot \text{ha}^{-1}$]
- f_{int} = fraction intercepted by crop canopy (default value = 0 for applications to bare soil or up to 0.5 for applications when a crop is present)
- depth = mixing depth [cm] (default value = 5 cm for applications to the soil surface or 20 cm where incorporation is involved)
- bd = dry bulk density [$\text{g} \cdot \text{cm}^{-3}$] (default value = 1.5)

The initial PEC is calculated in a similar way, according to the Phase II Tier A of the Guideline on the Environmental Risk Assessment of Medicinal Products for Human Use (EMA 2018). The equation, used for predicting the initial PEC of a chemical in the soil, after the first sludge application is:

$$\text{PEC}_{\text{SOIL}} = \frac{C_{\text{SLUDGE}} \times \text{Appl}_{\text{SLUDGE}}}{\text{Depth} \times \text{Density}}$$

Equation 2

The parameters are the following:

- PEC_{SOIL} = Predicted Environmental Concentration in soil after the first application [$\text{mg} \cdot \text{kg}^{-1}$ w. w.]
- C_{SLUDGE} = Concentration in sludge [$\text{mg} \cdot \text{kg}^{-1}$ w. w.]
- $\text{Appl}_{\text{SLUDGE}}$ = Yearly sludge application rate [$\text{kg} \cdot \text{m}^{-2}$]
- Depth = Mixing depth [m] (default value = 0.2)
- Density = Bulk density of wet soil [$\text{kg} \cdot \text{m}^{-3}$] (default value = 1700)

Given the long half-life of PAMs/PAAAs, the amount of such polymers applied to the soil is likely to remain relatively stable at least for the first months after application (see 2.1.1). The simple models for calculating the initial PEC, immediately after application therefore were considered adequate. In addition, the frequency of application is relatively low, i.e. not more than once every 1-2 years for sludges and even lower for SAPs, i.e. one



application conducted only every several years (data retrieved from the technical information of the specific products and/or communication with the manufacturers).

The FOCUS and the EMA models only differ in the default units and in the default values considered for soil density and soil depth. In addition, the EMA model integrates the concentration of the contaminant in the sludge into the equation and is then only valid for sludges. For the FOCUS model, the amount of the applied contaminant must be extrapolated first from its concentration in the sludge before applying the equation. However, for equal soil depths and densities, the two models provide the same result, so the initial PECs were calculated in this report only according to the FOCUS model and will be called simply “PEC” for the rest of this report. Also according to FOCUS, the values considered for soil depth are 5 and 20 cm, representing a scenario of no incorporation and incorporation in the soil, respectively, while the soil density is assumed to be 1.5 g/cm³. The PEC derived with the FOCUS model is expressed on a dry weight basis: unless specified differently, the PECs indicated in the rest of the report are to be considered in mg/kg of dry soil.

According to the Technical Guidance Document on Risk Assessment (European Commission 2003), effective Measured Environmental Concentrations (MEC) can be retrieved from the literature in case a PEC is not available. However, the methods for measuring environmental concentrations of PAM/PAA are scarce and their reliability is limited due to technical issues. A discussion about the availability of MECs is provided at the end of this section.

2.2.1 Linear PAM

2.2.1.1 Gravel sludge

Gravel sludge originates from gravel plants: when sand and gravel are washed and selected for the preparation of building materials, a fine mineral fraction and water are formed as a by-product (Behl and Bunge 2013). This raw material is treated with flocculants in order to separate the solid from the liquid phase, and the final gravel sludge can then be spread to agricultural fields, as a mineral soil conditioner. In Switzerland, gravel sludge has been provisionally authorized to be valorised as soil mineral improver (personal communication from FOAG). Because of their high content in calcium (CaO or CaCO₃), they are applied as liming fertilizers to counteract soil acidification (Sinaj and Richner 2017).

Gravel washing material produced by Swiss gravel plants is about 2 million tons per year (Behl and Bunge 2013). The contained fine fraction (< 63 µm) is extracted by means of flocculant application, resulting in a gravel sludge, that is not completely dry but has still a water content that is generally estimated to be around 30 % (otherwise it would not be a sludge but a powder). For this reason, flocculant concentrations, which are generally expressed on a dry weight basis, must be converted on a “wet” weight basis (i.e. based on the weight of the sludge having 30 % moisture content) in order to be consistent with the application rate of the sludge, that is expressed as well on the same “wet” weight basis. This was done for each of the following product cases, considering the assumption that all sludge products had an average dry content of 70 %. However, this is to be considered as an approximation, as dry content may be slightly different for each specific product (general values range from around 50 % to 80 %). When known, the exact dry content of a specific sludge should be integrated. Flocculants used for gravel sludge treatment are assumed to be mainly anionic PAMs (see 1.2.1).

1. Estimation of flocculant concentration in the sludge

Three cases were available, illustrating realistic concentrations of gravel sludge in Switzerland. For confidentiality reasons, the name of the products and the manufacturer were omitted here.

- A) Product A** is a typical anionic high MW PAM flocculant. In 2017, 650 kg of Product A were used to extract 4484 t sludge, corresponding to a flocculant concentration of 145 g/t



dw of sludge (personal communication with FOAG, based on considerations of several applicants for various types of gravel sludge). When considering a sludge having 70 % of dry content, this corresponds to **102 g of flocculants per t of “wet” sludge (ww)**.

- B) Product B:** Based on the previous considerations, the proportion of flocculant in the sludge was 162 g/t dw in 2018, i.e. **113 g/t ww**. This proportion was considered to be valid for three anionic PAM products, having similar properties.
- C) Product C:** The potential amount of PAM-based flocculants in gravel sludge is estimated to be around 0.1-2 kg/m³, based on respective data sheets of the polymers (Behl and Bunge 2013). When knowing the density of the sludge, it is possible to convert it to a range of concentrations, in mg/kg. However, density is likely to vary depending on the composition of the sludge. Only one example of gravel sludge product was available, for which the density is indicated in the technical information. The semisolid¹ form of this product has a density of 1.5 t/m³. Assuming that all gravel sludge used in the clarification process would have approximately the same density as this product, the estimated flocculant proportion based on the volume (0.1-2 kg/m³) corresponds to **67-1333 g/t ww**.

2. Application rates of the sludge

Application rates of gravel sludge vary depending on soil type and required lime addition and are generally based on the Principles of Agricultural Crop Fertilisation in Switzerland (PRIF) (Sinaj and Richner 2017). For the gravel sludge product available (see case 3), the amount of semisolid sludge indicated for farmland ranges between 3 and 10 m³/ha, depending on soil's clay content and pH. Given its mass per m³ (1.5 t), these rates correspond to **4.5 to 15 t of sludge per ha**. The PRIF also indicates various application methods and mentions both surface application and incorporation into the soil, when referring to mineral fertilizers (Sinaj and Richner 2017).

Other application rates recommended are 10 m³/ha for light to medium soils and 12 m³/ha for heavy soils for another specific gravel lime. However, sludge density is not available, so these volumes cannot be converted into t/ha. Depending on the density of this sludge, it is likely that the amount of flocculants applied to the soil could be even higher.

3. PEC derivation

The PEC was derived for each of the three product cases, considering minimal and maximal flocculant concentration for the case C. The application rate considered was both the minimal and the maximal dose indicated for the product available (4.5 to 15 t ww/ha). For each case, a best-case and a worst-case scenario was pictured. For the best-case scenario, we used the minimal application rate combined with incorporation (soil depth of 20 cm) in the model. For the worst-case scenario, we used the maximal application rate and no incorporation (soil depth of 5 cm). Minimal PECs ranged from 0.10 to 2.00 mg/kg and maximal PECs ranged from 1.34 to 26.66 mg/kg, depending on the product case. The results are summarized in Table 4.

2.2.1.2 Decarbonisation sludge

Similar to gravel sludge, another kind of sludge considered by FOAG can be used as liming material. This sludge is originating from the decarbonisation of cooling water used in nuclear power plants. Again, PAM flocculants are used to separate the solid phase from the aqueous phase, obtaining a sludge with high calcium carbonate content and a moisture content of approximately 30 %, which could then be applied as soil conditioner. One example of product was available and used for PEC derivation (case D).

¹ The other available form is liquid (density of 1.27 t/m³). Since flocculants bind to the solid particles and are used for dehydrating purposes. Here, we only considered the semisolid form, because it is more similar and thus comparable to the dehydrated products of other brands.



1. Estimation of flocculant concentration in the sludge

D) The anionic **flocculant product D** was used in the amount of approximately 20 t, to extract 11'000 t of decarbonisation sludge (personal communications with FOAG). This corresponds to a flocculant application of **1818 g/t dw** of the resulting sludge.

2. Application rates of the sludge

Similar to gravel sludge, the dosage depends on the soil characteristics. Based on the technical information, application rates for this product range from **1.5 to 10 t/ha**.

3. PEC derivation

As for gravel sludge, the PEC was derived considering the minimal and maximal application dose. The best-case reflected the minimal application rate and incorporation, while the worst-case considered the maximal application rate and no incorporation. The best-case for the decarbonisation sludge product considered was a PEC of 0.91 mg/kg (incorporation and minimal application rate) and the worst-case was 24.24 mg/kg (no incorporation and maximal application rate). The results are summarized in Table 4.

Table 4: PEC derived for the four sludge product cases, considering a minimal application rate of 4.5 and 1.5 t/ha, and a maximal application rate of 15 and 10 t/ha, for gravel sludge and for decarbonisation sludge, respectively

Product	Use	Flocculant proportion in the sludge (g/t ww)	Flocculant appl. rate (g/ha)		PEC (mg/kg)	
			Min. appl.	Max. appl.	PEC focus standard	
					Min. appl. and inc.	Max. appl. and no inc.
A	gravel sludge	102	457	1523	0.15	2.03
B	gravel sludge	113	510	1701	0.17	2.27
C (min. flocc. conc.)	gravel sludge	67	302	1005	0.10	1.34
C (max. flocc. conc.)	gravel sludge	1333	5999	19995	2.00	26.66
D	decarbonisation sludge	1818	2727	18180	0.91	24.24

2.2.2 Cross-linked SAPs

Cross-linked AA-AMD based polymers are applied as soil conditioners through direct mixing with the soil. Both application as water retention agent and as fertilizer coatings were considered and merged because of the similarity between the two product types (always in a powder or granular form) and the properties often being conferred by the same product.

1. Description of some SAP products and application rates

Nine product cases were considered, based on the information of actual hydrogels and combined hydrogel and fertilizer products. Such information was collected either from technical data sheets or the websites of the producer or provided directly as confidential information from the manufacturers. The products considered here are the following:

- E) **Product E** is a water retention hydrogel containing AA, AMD and K. The proportion of the polymer is 95 %.
- F) **Product F** is a water retention hydrogel belonging to the same brand as product E but composed only of a homopolymer of AA K and not AMD. The proportion of the polymer



was not provided, so we assumed it was the same as for the product E. According to manufacturer information, product E and F are designed to remain active in the soil for 1-3 years before degradation.

- **Application rates:** Technical data sheets suggest punctual application rates for both product E and F, from 8 g/8 L to 3 kg/m³ and extended application rates of 80 g/m² for a soil depth of 15 cm for product E. Other application rates found for product F were 4 kg/m³, and 15 to 65 kg/ha per year. Soil depth was not specified.
- G) Product G** is a water retention hydrogel made of K-PAA, containing only AA as monomer and without AMD, and according to the manufacturer, it is completely biodegraded after 8-10 years. The proportion of the polymer was not provided, we supposed that the hydrogel product is only composed of the polymer (100 %).
- **Application rates** are 3 g/L and 20 kg/ha, at variable soil depths.
- H) Product H** is a water retention hydrogel composed of AMD and AA. The dry matter content is indicated to be between 85-90 % and 88.5 %, depending on the reference. Assuming that the dry matter corresponds entirely of the polymer, a percentage of 88 % was chosen to represent the product. The time indicated by the manufacturer for complete biodegradation is up to 5 years.
- **Application rates** range from 10 to 40 kg/ha for big cultures, from 40 to 100 kg/ha for vineyards and orchards, and from 250 to 290 kg/ha for new lawns. Also, the product is applied by 1-2 g/L for punctual applications and 20 to 50 g/m² for extended applications. Other dosages indicated were 100 to 800 kg/ha for extended applications (once every 3 years) and 0.1 to 0.3 % for punctual applications (only once). When assuming the same density than for the product H (see above), 0.1 and 0.3 % correspond to 0.6 and 1.8 g/L.
- I) Product I** is a water retention hydrogel composed of a copolymer of AMD and K acrylate cross-linked material, biodegrading in the soil after 2 years, based on manufacturer information. The technical data sheet indicates a dry content between 87 and 100 %. Assuming that the product is only composed of the polymer, these percentages are retained as best- (87 %) and worst- (100 %) case.
- **Application rates:** suggested punctual dose is 5 g/5 L and extended dose is 50 g/m².
- J) Product J** is a combined water retention hydrogel and fertilizer, composed of K AA and AMD in the proportion of 5 % and according to the manufacturer, it is biodegraded after 3 to 5 years.
- **Application rates:** suggested punctual dose is 2 g/L and extended dose is 20 g/m².
- K) Product K** is a combined water retention hydrogel and fertilizer. It is composed of 29 % of a product that contains 95 % of a K PAA polymer. According to the manufacturer, it is biodegraded after 5 years.
- **Application rates:** suggested punctual dose are 3 g/L (without treatment of the upper layer) and 50 g/L, and extended application rate is 50 g/m² at a soil depth of 5 cm. However, it is indicated that no risk of overdosing exists, so the amount applied might be larger.
- L) Product L** is a combined water retention hydrogel and fertilizer, composed by 10 to 20 % of PAA. It biodegrades after 3 to 5 years, based on manufacturer information.
- **Application rates:** punctual application indicated by the product instructions is 6 g (10 ml)/L. A common application of 1 % and a maximal application of 2 % were also provided. Since 1 % corresponds to 10 ml/L that is equal to 6 g/L, 2 %



corresponds then to 12 g/L (assuming a density of 0.6 g/cm³). The instructions also suggest an extended application rate of 200 g/m² for soil depths ranging from 2 to 7 cm.

M) Product M is a combined water retention hydrogel and fertilizer. It contains K-PAA in the proportion of 41 % and according to the manufacturer, it biodegrades after 5 years.

- **Application rate** indicated in the instructions is 7 g/L.

2. PEC derivation

As can be noticed, some SAPs are applied punctually on limited zones (e.g. around a tree, plant or shrub) and their dosage is indicated, in g/L or kg/m³. In such cases, it is not realistic to consider application rates in g/ha and the PEC was simply derived by direct conversion of the indicated dosage into mg/kg, by considering a soil bulk density of 1,5 kg/m³ (FOCUS 1997). For these cases, the resulting concentration must be considered to be limited to a restricted area and soil depth is not taken into account (punctual application). In other cases, SAPs are applied extensively on a broad area (e.g. for new lawns or grasslands) and application rates are thus expressed in t/ha (extensive application). For this latter case, the FOCUS model was used for the PEC derivation. We adapted the soil depth in the equation accordingly, if information on soil depth was provided.

As for linear PAMs, the lowest and the highest PECs were retained for each product, considering minimal and maximal application rates and the polymer proportion (for both punctual and extended applications) as well as incorporation and no incorporation scenarios (only for extended applications), respectively. Best-case PECs ranged from 67 to 2000 mg/kg for punctual applications and from 3 to 253 mg/kg for extended applications. Worst-case PECs ranged from 67 to 9183 mg/kg for punctual applications and from 13 to 1333 mg/kg for extended applications (see Table 5).



Table 5: PEC derived for the nine SAP product cases, considering the application rates indicated for each product. Punctual PECs are derived by simple conversion from punctual application, expressed in mass per volume, into a soil concentration expressed in mass per mass, assuming a soil density of 1.5 g/cm³. Extended PECs are derived according to the FOCUS model. Best-cases reflect the lowest application rate and the minimal polymer concentration (for both punctual and extended applications) as well as incorporation into the soil (only for extended applications), while worst-cases reflect the highest application rate and the maximal polymer concentration (for both punctual and extended applications) and a no-incorporation scenario (only for extended applications)

Product	Description	Composition	Application rate		PEC punctual (mg/kg)		PEC extended (mg/kg)	
			Punctual	Extended	Best case	Worst case	Best case	worst case
E	hydrogel	95 % of K PAA	8g/8L; 3kg/m ³	80 g/m ²	633	2533	5	1013
F	hydrogel	95 % ¹ of K PAM	8g/8L; 3kg/m ³ ; 4 kg/m ³	80 g/m ² ; 15 kg/ha; 65 kg/ha	633	1900	253	1013
G	hydrogel	100 % ² of K PAA	3 g/L	30 kg/ha	2000		10	40
H	hydrogel	88 % ² of K PAM	0.6g/L; 1.8g/L	10 kg/ha; 290 kg/ha; 100 kg/ha; 800 kg/ha	352	1056	3	939
I	hydrogel	87 ² to 100 % ² K PAM	5g/5L	50 g/m ²	580	667	145	667
J	hydrogel combined with fertilizer	5 % of K PAM	2 g/L	20 g/m ²	67		3	13
K	hydrogel combined with fertilizer	29 % of K PAA at 95 %	3 g/L (upper layer not treated); 50 g/L	50 g/m ²	<551	9183	184	
L	hydrogel combined with fertilizer	10 to 20 % of PAA	6g/L; 12g/L	200g/m ²	400	1600	190	1333
M	hydrogel combined with fertilizer	41 % of PAA	7 g/L	NA	1913		---	

¹the polymer proportion of product F was not provided. We assumed that this was similar to the proportion of the product E, since they belong to the same brand.
²the polymer proportion was not provided. We assumed that this was 100 % of the dry content.

Taking into account the scarcity of data on the application of the considered products, a comparison with recommendations for other countries was conducted. Sanz Gómez et al. (2015) collected some application rates of SAPs, which were found to have positive effects on crop yield. One study indicated that in order to have a significant increase in water retention, it should be necessary to apply a SAP at a dose of 1 to 3 t/ha at field scale, although this is economically not reasonable (M. J. Zohuriaan-Mehr et al. 2010). On the other hand, data collected by Sanz-Gomez showed that positive effects on field crops were observed already at lower doses ranging from 5 to 60 kg of SAP per ha (see Appendix 1). The lowest value of all the recommended application rates is 5 kg/ha and was considered as a best-case for deriving a PEC. According to the FOCUS model, this resulted in a PEC corresponding to 6.67 mg/kg, assuming no incorporation and 1.67 mg/kg assuming incorporation. If considering instead the highest application rate of 3 t/ha, the PEC corresponded to 4000 mg/kg and 1000 mg/kg without and with incorporation, respectively.

Application rates for hydrogels are very variable and depend on several parameters, especially composition and the proportion of the polymer in the product, as well as application rates and depth of incorporation. Several combinations of PAMs and PAAs are possible and the exact composition of such polymers is not provided by the manufacturers. Also, if the product contains co-formulants, the contents of PAM/PAA is lower and the resulting PEC would also be lower. This variability limits strongly the feasibility of deriving a general PEC that could be representative for



a “common hydrogel product”. Given the diversity in the product properties and applications, a specific risk assessment should then be established for each product of interest, separately. Also, SAPs can be applied both on a limited area or on a wide surface. For the first case, the resulting concentrations are not representing the whole field but apply only to the treated area, because SAPs have a low mobility in soil. Finally, some manufacturers state that the recommended doses can also be exceeded and there is no risk of overdosing, since the products biodegrade completely. As a consequence, there are no known limitations to the application doses, thus PEC based on recommended dosing could underestimate the actual concentrations that can be found in the field.

2.2.3 MEC

Existing methods for measuring environmental concentrations of polymers like PAMs have often proved to be challenging, not standardized or to be biased by interference from dissolved organic carbon (Harford et al. 2011). Some methods have been used for measuring environmental concentrations of PAM, such as flocculation-based methods, or size exclusion chromatography combined with UV absorption (Lentz, Sojka, and Foerster 1996; Lu, Wu, and Gan 2003; Weston et al. 2009). However, these studies aimed at measuring PAM concentrations in soil pore water or in irrigation waters, following application by irrigation for erosion control which are scenarios not relevant for this report. Generally, PAM soil concentrations following application for erosion control remain below 10 mg/L in furrow water. However, for this purpose, PAM is commonly dissolved and applied with irrigation water (Sojka et al. 2007; Weston et al. 2009) and its fate is likely to be different than the one considered in this review (i. e. more transfer to water and less sorption to soil, as well as different application rates). Due to the strong adsorption of the polymers to soil particles, the detection of PAM concentrations in the soil remains challenging and the most efficient technic is the use of ^{14}C -radiolabelled polymers (Hennecke et al. 2018). The only MEC for PAM similar to our case was the one measured by Hennecke et al. (2018), who studied the field application of a sewage sludge, dewatered with a linear cationic PAM. The authors applied 2.0 g of ^{14}C -PAM in 660 g sludge dw per m^2 , which corresponded to a flocculant concentration of 3030 g/t of sludge dw, and an application rate of 20000 g of PAM/ha. One day after treatment, the measured radioactivity was 1657 Bq / g soil dw in the first 10 cm of depth. Knowing that 329.9 MBq corresponded to 3.5 g of ^{14}C -PAM (indicated by Hennecke et al. 2018), then the amount of ^{14}C -PAM detected after one day would be $1.76 \cdot 10^{-5}$ g/g soil dw, which corresponds to 17.6 mg/kg. These numbers are in the range of the PECs calculated in this report for linear PAMs.



3 Effect assessment

Since polymers are not covered by most chemical regulations, toxicity databases are mostly inexistent (Reinert and Carbone 2008). Consequently, PAMs and PAAs do not require a proper ecotoxicological assessment (see 1.2). Various PAMs/PAAs exist and commercial products are used under different types of formulation, thus information about their environmental impact is often proprietary and rarely available from the manufacturer (Rowland, Burton, and Morrison 2000). Due to their large molecular size they do not pass biological membranes, further, high molecular weight polymers are generally considered to be chemically inert and therefore mainly non-toxic (Smith and Oehme 1991). Most reviews were based on these considerations and referred to few available toxicological data, to support the safety of PAMs and PAAs (Sojka et al. 2007; Hüttermann, Orikiriza, and Agaba 2009). Given their supposed low toxicity, evaluation on the environmental impact of such polymers has mostly focused on their degradation. The main concern was the potential release of AMD and AA monomers, which is commonly assumed to be low (see 2.1.1.3). Pure PAM products are expected to be non-toxic and their content in residual monomers coming from the production is kept below legal limits (Caulfield, Qiao, and Solomon 2002). Since toxicity of AMD and AA is relatively well known (see 1.3), and supposing that degradation products are either released at non-relevant concentrations or not enough studied (see 2.1.1.3), this chapter focused mostly aquatic and terrestrial ecotoxicological data, for the polymeric products, linear PAM and cross-linked PAA. For each polymer structure and each environmental compartment, where possible, an approximation of a Predicted No Effect Concentration (PNEC) is derived, following the method described in the Technical Guidance Document on Risk Assessment, proposed by the European Commission (European Commission 2003). This method proposes the lowest ecotoxicological threshold level found in the literature and the application of an assessment factor, which is based on the amount of reliable data available and the type of ecotoxicity tests performed.

3.1 Linear PAMs

3.1.1 Effects on aquatic organisms

Given their high-level use in water treatment, extensive literature about the impact of linear AMD-based flocculants on aquatic species is available. Most studies focused on the generic use of polymeric flocculants in water treatments and on the potential impact of polymer releases in water effluents. Fewer studies investigated the effect of PAM use in agriculture for erosion/infiltration control.

Given the high number of polymers existing on the market, ecotoxicological thresholds for linear PAM can vary considerably in the literature. For instance, the Auckland Regional Council reported EC50/LC50 values for freshwater species ranging from 0.04 mg/L to more than 4000 mg/L for polyelectrolytes (ARC 2012). Polyelectrolytes are charged polymers, which can be both coagulants (mainly polyamines) and flocculants (mainly PAM). In this chapter, the available literature on linear PAM flocculants was reviewed. Various ecotoxicological effect concentrations were collected, ranging from 0.06 mg/L to 3440 mg/L (see Appendix 2).

A major factor driving the toxicity of generic polyelectrolytes is ionic state, with toxicity increasing with increasing charge density (ARC 2012). Earlier studies showed that cationic polymers bind strongly to fish gills, which have a negative surface charge. This limits gas exchange of fish, which can lead to death by suffocation (Biesinger et al. 1986). This mechanism is typical for most cationic polyelectrolytes, including linear cationic PAM. A study published by Dow Chemical Company (1970), showed 100 % mortality of fish at 10 mg/L after 72 h for a cationic PAM formulation. Biesinger et al. also showed the acute toxicity of a cationic PAM in two lake trout species (1976) and successively described in detail the mechanism of gill damage caused by cationic polymers (1986).



The effect of charge density in cationic polymers on increasing toxicity to fish, was further confirmed by Hall and Mirenda (1991) and Goodrich et al. (1991). Cationic PAMs were found to cause acute toxicity also to other aquatic species than fish, such as algae and crustaceans, especially daphnids (Biesinger et al. 1976; Hall and Mirenda 1991; Rowland, Burton, and Morrison 2000; Beim and Beim 1994). Most of these publications focused on the toxicity of polyelectrolyte flocculants used in wastewater treatment, with residual flocculants, occurring at high concentrations in the effluents of industrial wastewater treatment plants. However, as the flocculants bind to solid particles, their toxicity was considerably reduced by the addition of suspended solids, such as clay (Biesinger et al. 1986) or organic matter (Biesinger et al. 1976), which limit their bioavailability to aquatic organisms. Therefore, the authors agreed generally that the bioassays conducted with standard waters, as recommended in the most guidelines (e.g. reconstituted waters) tended to considerably overestimate the toxicity of the polymers. In a more realistic situation of water effluents, the high load of suspended solids, such as waste, pollutants, or organic carbon, would tend to neutralise their impact on aquatic species by reducing bioavailability (Hall and Mirenda 1991; Goodrich et al. 1991). The risk of cationic polymers to aquatic species should then be evaluated, only investigating the residual amount, which is still present in the effluents after flocculation (Dow 1970). In the meantime, the use of cationic polyelectrolytes has been reduced and generally limited to close-loop systems, in order to avoid transfer to surface waters (Kerr et al. 2014).

On the other hand, anionic polymers are commonly assumed to be non-toxic to fish and many freshwater invertebrates (Barvenik 1994; Entry et al. 2002; Liber, Weber, and Lévesque 2005; Krauth et al. 2008; Weston et al. 2009; Dow 1970; Kerr et al. 2014). As a consequence, they have been considered environmentally safe and are commonly used for particle stabilisation, to form aggregates or for liquid-solid phase separation (ARC 2012). However, some earlier studies indicated evidence of anionic PAM acute toxicity to fish (Biesinger et al. 1976) and to *Daphnia pulex* (Hall and Mirenda 1991). The latter experiment suggested that generally the toxicity of polymers to *Daphnia* was mostly driven by chemistry, rather than charge density. In fact, among various anionic PAM formulations, all of them showed very low LC50s, ranging from 0.06 mg/L to 0.66 mg/L. The mode of action for crustaceans was still thought to be mechanical, resulting in physical entrapment. Care should be taken, when considering these values, because the formulation of the PAMs was not specified in detail and was indicated to be an emulsion. As indicated later, additional ingredients present in some emulsions can increase the toxicity of the product.

Adverse effects of anionic PAMs were shown to occur also in chronic exposures (Beim and Beim 1994). The authors exposed a range of aquatic organisms to five differently charged PAM flocculants, in a pure powdery form, up to 3 months. Although the most toxic were the cationic species, followed by non-ionic and finally anionic, all the tested polymers indicated chronic toxicity. The most sensitive to anionic PAM were *Daphnia magna* and algae and adult fish to a lesser degree, reporting vital concentrations of 0.01 mg/L for the first two and 5.0 mg/L for the latter. The authors concluded that the tested PAM flocculants should be all considered as micropollutants and that their use should be regulated, by giving the priority to less bioactive compounds and by controlling the residual polymer content in water effluents. The methods and the endpoints of this study were not defined in detail (in particular, the endpoint "vital concentration" was not clearly defined), which limits the reliability of toxicity values for an effective risk assessment. Nevertheless, this study was one of the first indicating chronic toxicity of anionic PAMs, and describing their generic mechanical effects to aquatic organisms.

Based on most recent publications, there is a growing evidence that anionic PAMs can lead to toxic effects on freshwater organisms, especially in chronic exposures. Weston et al. (2009) investigated the impact of linear PAM in various formulations used for erosion control in agricultural fields on aquatic species. Laboratory bioassays with granular and almost pure (97 %) PAMs did not show a significant lethal or sublethal effects on most of the tested species, exposed at concentrations comparable to realistic application rates (1-10 mg/L). The only sensitive species was *Ceriodaphnia dubia*, showing an EC50 for reproduction of 5.1 mg/L, after exposure to a pure



granular PAM over 6-8 days. Also, PAM in an aqueous formulation slightly impaired the growth of algae, after 96 h (IC₅₀ = 14.6 mg/L). On the other hand, when PAM was used as an oil-emulsion formulation, marked toxicity to most species was due to co-formulants. The effect of the anionic active ingredient PAM was suggested to be mechanical, caused by the increased viscosity of water, which induced stress to small organisms. In addition, PAM was found to flocculate small particles, including algae and other food sources, making them less available. This could explain why daphnids and algae were impacted negatively by the polymer.

Since PAMs bind strongly to soil particles, toxicity of oil-based products was also tested in sediment bioassays. These were showing contrasting results, the presence of sediment increasing PAM toxicity to *Hyalella azteca* and reducing it for *Chironomus dilutus*. Finally, field trials demonstrated toxicity of oil-based emulsions in incoming irrigation water and it was lower, but still detectable, further downstream.

The sensitivity of *Daphnia magna* to anionic PAM was confirmed successively by Acharya and co-workers (2010). After 32 days of continuous exposure of *Daphnia magna* to a linear anionic PAM pure formulation, a NOEC of 0.5 mg/L (LOEC 1 mg/L) for growth and a NOEC of 5 mg/L (LOEC 10 mg/L) for fecundity and onset to reproduction were derived. This highlighted the importance of chronic bioassays to evaluate the ecological stress to daphnia. Similar to the previous studies, the authors observed that the flocculant increased water viscosity, which inhibited the ability of small organisms to move and to filter and consume food, resulting in a negative impact on their overall fitness.

The ecological impact of an anionic PAM flocculant block formulation was investigated further by Harford et al. (2011) on five tropical freshwater species. The authors found that the PAM formulation impaired the growth of hydra (*Hydra viridissima*, EC₁₀ = 80-60 mg/L, PAM concentration expressed on a total carbon content basis, C TOC). Stronger negative effects on the reproduction of the cladoceran *Moinodaphnia macleayi* (EC₁₀ = 4 mg/L C TOC) were detected. Although chronic toxicity on growth was not observed in duckweed and algae and the survival of fish larva was neither affected, the algae were flocculated and the locomotion of fish larva was greatly inhibited. Contrastingly to the results of Weston et al., the study also showed that toxicity was primarily due to the pure flocculant, rather than co-formulants and that PAM alone was generally more toxic than the formulation. This can be explained by the fact that the carrier did not contain other toxic ingredients, as in the case of oil-based emulsions.

Harford and co-workers proposed a derivation of Protective Concentrations (PC) for the PAM flocculant, according to the probabilistic risk assessment method, based on the construction of a Species Sensitivity Distribution (SSD) (Posthuma, Suther II, and Traas 2002). The protective values were calculated, based on the effective chronic concentrations found in their study and on data found in the literature on 11 species in total. The resulting PC protecting 95 % of species were 5 mg/L for the flocculant block formulation, analysed in their study, and 1 and 0.4 mg/L for PAM alone (values of the single study and the combined data, respectively). Based on such low PC, Harford et al. supported the hypothesis that under chronic exposure cladocerans are particularly sensitive to anionic PAMs.

The indirect impact of residual polymers contained in fertilizers is rarely assessed. Hennecke et al. (2018) investigated a cationic PAM, which was present as a residual in sludge which was used as soil conditioner. However, the concern about the impact of the polymer was limited to its environmental fate, especially its degradation, based on the assumption that PAM itself was non-toxic to the environment.

A similar study was conducted by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES), in order to evaluate the ecological impact of a sludge amendment, which was contaminated by PAMs, ferric chloride and a bacterium potentially dangerous for humans (Anses 2010). Ecotoxicological tests on lixiviates of this sludge indicated acute toxicity to daphnids and chronic toxicity to algae. However, it is not clear whether the observed toxicity was caused by PAMs directly or by other substances, such as ferric chloride or the detected bacteria. A following report by Anses (2012b) highlighted the importance of testing the effect of



the same sludge by means of soil and water bioassays (testing the lixiviates of soil test), in order to better evaluate the long term toxicity caused by the sludge and/or by potentially mobile PAM degradation products, which could transfer to water through lixiviation.

3.1.2 Effects on soil organisms

In contrast to aquatic species, data on the toxicity of linear PAM to soil organisms is very limited and most publications are limited to effects on soil microorganisms or plants.

PAM effects on soil microorganisms have been shown to be variable. PAM was reported to both decrease and increase soil microbial biomass (Kay-Shoemake et al. 1998; Orts, Sojka, and Glenn 2000; Watson et al. 2016). Sojka et al. (2006) demonstrated that, although PAM exposure decreased the microbial biomass, the microbial metabolic potential was not affected. However, no data from standardized laboratory ecotoxicological bioassays are available, as suggested in international guidelines, such as carbon or nitrogen transformation tests, following OECD protocol (OECD 2000a, 2000b). Therefore, the available results cannot be used for a proper PNEC derivation and the general impact of PAM on soil microorganisms remains variable and difficult to evaluate.

Effects on plants were reviewed recently by Düzyol (n.d.), who reported that only few studies are available (Kuiuhara and Watanabe, 1976; PFA, 1978; Kuboi and Fujii 1984). Adverse effects on turnip roots and *Clamydomonas spp.*, or on Chinese cabbage and radish were caused by cationic PAM species, following PAM application ranges of 25 mg/L to 2000 mg/kg, respectively (Kuboi and Fujii 1984). To our knowledge, toxicity of anionic PAMs to plants has not been reported. The literature review composed by Seybold (1994) concluded that linear PAMs were generally not toxic to plants, based on a small number of available studies.

Concerning the impact of PAMs on soil invertebrates, only two publications were found. One report published at the Ecotoxicology Laboratory in the Landcare Research institute of New Zealand, investigated the acute effect of linear PAM on earthworms (*Aporrectodea caliginosa*) and woodlice (*Porcellio scaber*) (Garcia 2005). *P. scaber* was not significantly affected in terms of mortality and biomass change, when exposed to food (cow dung), contaminated with up to 5000 mg/kg dw of PAM. For *A. caliginosa*, the authors reported that growth was not inhibited up to an exposure concentration of 1000 mg/kg, while it was impacted from 2000 mg/kg upwards. No mortality, in turn, was found up to 2000 mg/kg, but reached 100 % at 4000 mg/kg. The author pointed out that at 4000 mg/kg PAM, the soil appeared dryer, which could have influenced the survival of earthworms. This hypothesis was rejected by repeating the test at a concentration of 4000 mg/kg in a moister soil (increase in 10 %) leading to the same results. Although statistical analysis was not provided, which limits the reliability of the study, the results obtained from this study suggest NOEC values of 1000 and 2000 mg/kg for growth rate and mortality, respectively. Unfortunately, the ionic state of the PAM was not indicated.

The second paper available was a Chinese publication, which investigated acute and chronic effects to the earthworm *E. fetida* of a PAM flocculant commonly used for waste water treatment (Feifan, Qin, and Zhenjun 2012). However, the charge and properties of PAM are not specified. Consistent with the previous report, mortality was not observed up to an exposure concentration of 2000 mg/kg, but reached 100 % at 4000 mg/kg in the acute test (14d). Again, the authors suggested that mortality of worms was due to the consolidation of the artificial soil caused by PAM. However, they did not investigate this hypothesis further. In chronic bioassays, the growth rate of *E. fetida* was not reduced up to the highest concentration tested (2000 mg/kg). On the contrary, some high PAM concentrations seemed to increase growth rate. The authors suggested that soil quality could have been improved by an increased water retention, which was induced by PAM. However, this is questionable since linear PAM are not capable of absorbing huge amounts of water as opposed to cross-linked PAMs and contradicts previous observations of soil appearing drier at similar PAM concentrations. On the other hand, over a 42 day-exposure, a clear dose-response relationship was observed between PAM concentration and inhibition of worm reproduction. A clear inhibition of reproduction could be noted at a concentration of 250



mg/kg (see Table 6). The NOEC was determined at 50 mg/kg. The authors concluded that, while no acute toxicity occurred, a chronic effect on the reproduction of earthworm was observed and that an ecological risk exists, following the application of sludge treated with PAM flocculants. In the same year, a report realised for ANSES, reported that the actual literature disposes only of little data on acute exposures, these indicating low ecotoxicological effects of PAMs to aquatic and soil organisms, while information about effects of chronic exposure is not available (Anses 2012c).

Table 6: Number of juvenile per worm produced after 42 days exposure to PAM (Feifan, Qin, and Zhenjun 2012)

	PAM concentration (mg/kg)				
	0	10	50	250	500
Mean value	3.67	3.30	3.17	0.70	0.30
Standard deviation	0.208	0.200	0.208	0.200	

3.1.3 PNEC determination

3.1.3.1 PNEC for water

The presented PNEC derivation is based on anionic PAMs, because they are assumed to be the most frequently used in sludge treatment. According to the TGD (European Commission 2003), when chronic toxicity NOEC values for at least three trophic levels are available, an assessment factor of 10 can be applied. TGD also indicates that a long-term EC10 can be considered as a NOEC, if it is obtained by extrapolation using appropriate statistics (e.g. Probit analysis). In addition, an assessment factor of 10 is justified if the species tested, having the lowest value, can be considered to represent one of the more sensitive groups (European Commission 2003).

Among various available, the lowest chronic NOECs for fish are 75 mg/L for *Salvelinus namaycush* (lake trout) and 0.5 mg/L for *Daphnia magna*, while a IC10 of 40 mg/L was the available chronic threshold for *Chlorella sp.* (unicellular green alga) (Liber, Weber, and Lévesque 2005; Acharya, Schulman, and Young 2010; Harford et al. 2011) (Appendix 1). The IC10 value of *Chlorella sp.* was obtained by linear interpolation (Harford et al. 2011) and is considered reliable. The lowest threshold (NOEC = 0.5 mg/L) is from *Daphnia*, which is indeed the most sensitive species according to the collected data. When divided by an assessment factor of 10, this results in a PNEC of 0.05 mg/L. This value is within one to two orders of magnitude of the protective concentrations of 1 and 0.4 mg/L for PAM, derived by Harford et al. (2011), based on the sensitivity of *Daphnia magna*.

3.1.3.2 PNEC for soil

According to the TGD (European Commission 2003), if only one test result with soil dwelling organisms is available, the PNEC for soil should be calculated using both the assessment factor and the equilibrium partitioning method. The highest $PEC_{soil}/PNEC_{soil}$ ratio of the two $PNEC_{soil}$, derived with the two methods, is then chosen for the risk characterization. However, the TGD highlights that the equilibrium partitioning approach may not be suitable for substances with a specific mode of action or for species that are exposed primarily through food, and that it does not consider the effects of chemicals that are adsorbed to soil particles and taken up by ingestion (European Commission 2003). Since PAMs strongly bind to the soil and sorption is mostly irreversible, they are indeed likely to be ingested. For this reason, the PNEC for soil is calculated only based on the assessment factor and care should be taken with regard to the derived value.

According to Table 20 of the TGD, if only one NOEC for long-term toxicity tests is available, an assessment factor of 100 should be used (European Commission 2003).



Based on the lowest reported NOEC of 50 mg/kg (see Table 6), the derived PNEC for soil is 0.5 mg/kg.

However, it is not known if this value is applicable for anionic or cationic PAMs, which considerably limits its use in risk assessment.

3.2 Cross-linked SAPs

3.2.1 Effects on aquatic and soil organisms

When the environmental safety of superabsorbent hydrogels is investigated, the available publications tend to refer mainly to the degradation behaviour of these substances. The concern about their toxic impact has been generally limited to potential release of toxic by-products, which is commonly assumed to be low (see 2.1.1.3). Consequently, very few studies have been found which report ecotoxicological tests to either soil or aquatic organisms. A common assumption is that cross-linked SAPs are biodegradable and thus eco-compatible. Products made of PAM are indicated to be biodegraded completely after a few years and therefore to not pose any danger to the environment. Products made of PAAs are generally assumed by manufacturers to be non-toxic because they do not contain AMD monomers and should be degraded completely in soils as well (information retrieved from the manufacturers, such as website and personal communications). Sutherland et al. (1997) reported that “in-depth ecotoxicological testing has provided no evidence for significant adverse effects of such polymers (i.e. cross-linked polymers of acrylic acid and co-monomers such as acrylamide, nda.) to marker organisms in water, or plants and birds, due to their chemical inertness”. However, no references were given in their publication to effective ecotoxicological bioassays on the polymers. Successively, Hüttermann et al. (2009) stated that “all published studies on the toxicity of SAPs on an acrylate basis have shown that these substances have a positive toxicological profile (i.e. low toxic effects, nda) and can be considered environmentally compatible”. Nevertheless, most sources referred in their review, indicated bioassays on animals, in the context on human toxicity (McGrath et al., 1993; Haselbach et al., 2000; Fiume, 2002; Garay-Jimenez, 2008). One publication focused on aquatic life, based on the effect of high volume acrylate and methacrylate residuals, such as acrylic acid, butyl acrylate, ethyl acrylate, methacrylic acid and methyl acrylate. These compounds can be residuals from household products, which are discharged from municipal wastewater treatment plants (Hamilton, Reinert, and McLaughlin 1995). Although the study found that no risk to aquatic organisms was to expect from release of the above cited acrylate and methacrylate residuals, cross-linked SAPs have a different chemistry and structure than the ones studied and their potential ecotoxicology was not mentioned. In the same review of Hüttermann et al. (2009) a few publications were quoted, which indicated no adverse effect to the soil microbial community following the use of superabsorbent polymers used as fire retardants in forest (Basanta et al. 2002; Díaz-Raviña et al. 2006; Lee, Kim, and Ryu 2008). Cross-linked gels are commonly considered as inert substances and have been found to be relatively biodegradable, in a similar way as organic matter (see 2.1.1.2). For all these reasons, Hüttermann et al. (2009) concluded that SAPS are considered environmentally safe, with degradation rates similar to those of litter entering the humus cycle and due to their low toxicological profile.

However, earlier studies had highlighted detrimental effects of hydrogels on some plants. In some cases, the use of SAPs was found to inhibit the growth of some woody plants, such as pine bark (Keever et al. 1989), ligustrum (Ingram and Yeager 1987), European birch (Tripepi et al. 1991), or blueberry (Austin and Bondari 2019), at hydrogel concentrations of 1.2 kg/m³ or higher. Data published by Chen et al (2017) indicate that hydrogels can in some cases inhibit root growth and decrease plant biomass, with stronger impacts at higher polymer doses. Although SAPs are used to maintain water availability for plants, this property has been questioned by a few studies. Authors suggested that these polymers could sometimes rather compete with plants for water, and thus reduce the water availability for the roots (Chen et al. 2016). Chen et al. (2017) reported negative effects on the growth of maize seedlings, which were cultivated in a growing medium



composed of 150 g of water-saturated hydrogel (both K and Na-PAA). In a previous study, the authors suggested that the mechanism of maize crop damage by superabsorbent acrylate polymers was primarily due to AA present in the polymer (Chen et al. 2016).

Concerning microorganisms, a recent publication (H. Wang et al. 2019) reported that SAP application of 0.1 % dw to soil changed the ecological bacterial diversity, by promoting the growth of certain species and reducing the amount of others. They also found that when the soil was water-saturated, SAPs could release some substances, such as methanesulfonyl chloride, long-chain amides and esters, which could lead to a negative impact on the environment. A more recent study showed that the effect to microorganism community was negligible for a PAA waterborne coating (Dong et al. 2019)

To our knowledge, these are the only published studies assessing the ecotoxicological impact of cross-linked PAMs/PAAAs. Unfortunately, none of them could provide proper dose-response descriptions and valid ecotoxicological thresholds, which hinders the establishment of a PNEC. The lowest data available indicated that some woody plants can be inhibited by SAP concentrations $\geq 1.2 \text{ kg/m}^3$. If assuming a soil bulk density of 1500 kg/m^3 , this value can be interpreted to be around 800 mg/kg . More data is available on effects of other polycarboxylates, which are used as ingredients in detergents, reporting various thresholds, especially for aquatic organisms, which indicate no risk to both aquatic and soil organisms (ECETOC 1993). However, the investigated polymers are either homo-polymers of AA or co-polymers of AA and maleic anhydride. Although composed of the same monomer, polymers used as hydrogels in agriculture are mainly co-polymers of AA and other monomers than maleic anhydride (see introduction). Thus, the mentioned findings do not generally apply for the substances and usages focused on in this study.

3.3 Conclusion

3.3.1 Linear PAMs

Information on the toxicity of PAMs focuses mostly on the water compartment. Cationic polymers are known to pose a substantial hazard to aquatic life and their use is limited to closed systems. On the other hand, anionic PAMs were supposed to be safer for water species and to cause no hazard to the environment when applied at the recommended doses (Barvenik 1994; Sojka et al. 2007). The assumption that suspended solids in waters tend to buffer PAMs' impact on aquatic life has been generally extended for all ionic states of PAMs, as well as for the soil compartment (ARC 2012; Sojka et al. 2007). However, evidence of anionic PAMs being hazardous to aquatic species has been provided in various long-term exposure laboratory bioassays. The toxicity depends on polymer characteristics such as chemistry, and affects mainly small organisms like crustaceans, especially *Daphnia*, and algae. As for cationic PAMs, the mode of action is also mechanical, but is rather induced by increasing media viscosity and the flocculation of solid particles. Finally, the formulation of the PAM flocculant can change considerably the impact of the polymer. For each product, it should be investigated whether a potential toxicity originates from the pure polymeric substance or from some co-formulant.

The toxicity of linear PAMs to soil organisms is difficult to assess, given the limited information. PAMs seem to have little effect to soil microorganisms and to plants, especially anionic PAM species. Data on soil invertebrates is even more limited. Similar to water, the attraction of PAM to solid particles is expected to decrease the bioavailability to soil organisms and thus to reduce their impact. Nevertheless, a study indicated a strong impact on reproduction in earthworms and has provided the derivation of a PNEC of 0.5 mg/kg . Unfortunately, it is not known whether cationic or anionic PAM was used. It is difficult to derive the mode of action of PAM on soil invertebrates from the aquatic compartment. Because of strong sorption of PAM to soil particles, the exposure could be via soil ingestion, rather than direct contact (e.g. attraction of polymers to biological membranes). Since evidence of chronic toxicity of PAM to earthworms exists, further



studies with the same species as well as other standard soil organisms are necessary in order to better assess the impact of PAMs.

The derived PNECs for water and for soil indicated that some species are particularly sensitive to linear PAM, first daphnids (PNEC = 0.05 mg/L) and secondly earthworms (PNEC = 0.5 mg/kg).

3.3.2 Cross-linked SAPs

Ecotoxicological data of cross-linked gels are mostly inexistent, especially for aquatic species. These polymers have generally been assumed to be inert, biodegradable and to promote the growth of plants and of certain bacterial communities in the soil. Compared to the strong literature evidence on the benefits to plants and microorganisms posed by these polymers (see 1.2.2), the studies reporting adverse effects on the same organisms are limited and focused on specific field cases/species. A PNEC derivation is difficult due to the lack of appropriate thresholds, the lowest value of 800 mg/kg was derived from specific forest plants. However, these observations have raised some concern about the use of hydrogels and opened the way to further research. Proper investigation of the impact on soil invertebrates is still lacking, which is essential for making a reliable risk assessment.



4 Discussion / risk assessment

This chapter aims at comparing the main considerations expressed concerning exposure and effect of the studied polymers and at discussing potential consequential risks. The data gaps are also highlighted.

4.1 Linear PAMs

Linear PAMs are used for dewatering some industrial by-products, such as gravel or decarbonisation sludge, that are afterwards used as soil improvers. These flocculants are thus expected to be present in the final product when it is applied to the soil. It is difficult to estimate with precision in which concentrations such flocculants can be found in the soil, firstly due to the lack of appropriate models. Also, the properties (e.g. calcium content, density, dry matter content) of gravel sludge can vary resulting in different application rates. Some approximations have thus been necessary in order to derive PECs. First, models valid for pesticides and/or medicals were assumed to be valid and only the initial concentration right after the application was considered. In addition, the amount of flocculants present in the sludge was calculated, based on the few available examples although there might be other brands of sludge with different properties. If a better knowledge about flocculant amount entering to the soil is required, each product should be evaluated in detail, considering its specific properties and application rates. Also, a better model considering the environmental fate of water soluble polymers should be established. Finally, some of the calculated PAM concentrations in the sludge were derived from the assumption that all flocculants used for the dewatering process actually remain in the final product. Hennecke et al. (2018) observed a loss of 28 % of the initial flocculant amount after treatment of a sewage sludge with cationic flocculant. Further studies measuring the actual amount of flocculant in the final sludge would then be useful. Keeping in mind these approximations, the PECs derived for linear anionic PAMs range from 0.10 to 2.00 mg/kg, assuming incorporation into the soil and from 1.34 to 26.66 mg/kg, assuming no incorporation (see Table 4). The variability of such values is due to the use of different models and different flocculation concentrations considered. Once entered into the soil, such flocculants are expected to remain for a long time at such concentrations, given their high half-life, high sorption, and low mobility.

Since they are water soluble, a part of linear PAMs could leach to waters. This is expected to be a minimal part, given their strong adsorption to soil particles. However, more exposure data about realistic PAM concentrations in water would be needed, in order to better quantify the proportion of polymers leaching to the waters. Linear PAMs have been shown to be toxic to some aquatic species, and the impact depends on various parameters, such as polymer chemistry, charge density, or formulation. Since the PAMs considered here are mostly anionic, their leaching to waters could lead to negative effects to the most sensitive species, such as daphnids or algae. The PNEC derived, based on the response of most sensitive species (0.05 mg/L, derived from growth inhibition of *Daphnia magna*) would suggest a high risk for water. Nevertheless, the amount of PAM transferred to water should be low. In addition, it is commonly agreed on that toxicity thresholds based on laboratory bioassays realised in standard water tend to overestimate the actual toxicity of PAM under realistic field conditions. This is due to the tendency of PAM to bind to suspended solids which are naturally present in the water, limiting its bioavailability to aquatic organisms. Despite its potential high toxicity to water, exposure of organisms to PAM should be therefore limited, suggesting that the risk of the polymer for aquatic organisms should be low. But, proper and reliable PEC calculation (even MEC data if possible) are needed to verify this assumption. Nevertheless, the strong adsorption of linear PAMs to soil particles can potentially lead to transfer to the sediment compartment. Although this is expected to be limited, as anionic PAMs are used in purpose for limiting sediment run-off and turbidity (Sojka et al. 2007), some transfer to sediments cannot be excluded with certainty. The knowledge about PAMs effect in this compartment is still limited and shows contrasting results (Weston et al. 2009), thus bioassays on sediment organisms could be an additional instrument for risk assessment.



Some concern still exists on the possibility that some intermediate products of the degradation of PAM could leach into waters. In particular, AA is highly soluble and mobile, as well as highly toxic to aquatic species (see 1.3.1). In order to assess the risk to aquatic species better knowledge on the degradation by-products of PAMs is necessary.

Most of the flocculant amount applied with the fertilizer would probably remain in the soil (see 2.1.4). Given the high half-life of PAMs in the soil and their persistence (see 2.1.1.4), the calculated concentrations are then likely to decrease only slowly. PAM concentrations, as calculated with PEC models, would thus remain stable for a long time (at least several months) in the soil and, since fertilizers containing PAMs are applied several times, accumulation is also likely. Consequently, soil organisms are expected to be exposed for a long time to such polymers. Available studies about ecotoxicological effects of linear PAMs to soil are not sufficient to establish a valid risk assessment. A few publications suggested a low toxicity to soil species, especially in the short-term. In addition, PAMs bioavailability is expected to be low, due to strong sorption to soil particles. An indirect effect is likely at very high doses of PAM flocculants (e.g. several millions of mg/kg), which can induce changes in soil structure because of particle aggregation and compaction. It is not clear whether these changes can be positive (e.g. better water retention) or negative (e.g. soil compaction) to soil organisms. However, according to the PECs derived for flocculants, it is unlikely that such high concentrations occur in the environment (see 2.2.1). Although adsorption limits the bioavailability, PAM can be ingested by soil organisms. One publication reported chronic toxicity of a linear PAM of unknown charge to earthworms. This value was used for deriving a PNEC of 0.5 mg/kg, based on reproduction response. The ratio between PEC and PNEC calculated in this study is greater than one for all derived PECs excepting one (see Table 7). This consideration would require that further degradation testing would be needed on the considered polymer, in order to better refine the risk assessment (European Commission 2003). As discussed above for water, the degradation products of PAM in the soil still need some clarifications. Literature generally focused on AMD releases and considered that the risk to soil organisms was low because AMD is produced at negligible amounts and, even if it is released, it is rapidly biodegraded. However, the risk of other potential toxic monomers (e.g. AA) is rarely considered. Globally, the literature about the effect of PAMs and their degradation behaviour in soil is then too limited to derive proper critical values. The PEC/PNEC ratio derived by using the only available PNEC based on the effects of a linear PAM to earthworms indicates that an ecological risk exists. However, the characteristics of the polymer studied were not known, and, as it was shown for water, especially charge density is a major factor driving the PAM effect to main organisms. The PEC/PNEC ratio can thus not be used for assessing the risk of the flocculants concerned in the present study. Nevertheless, a risk cannot be excluded. Targeted ecotoxicological bioassays in the laboratory with a range of species representing all trophic levels of soil are required to further investigate this hypothesis, taking into consideration the properties of PAMs (especially charge). Additionally, further studies on their degradation behaviour and products under field conditions, for instance by using ¹⁴C-radio-labelled polymers, would be useful. Furthermore, experiments of transfer and impact at a mesocosm scale under realistic environmental conditions would be of a plus for depicting the risk of these products.

Table 7: Risk quotient (RQ = PEC/PNEC ratio) derived for the soil compartment for linear PAMs. RQ in red indicate a possible risk for soil organisms

		PEC (mg/kg)	PNEC (mg/kg)	RQ
gravel sludge	Best-case	0.10	0.5	0.20
		2.00	0.5	4.00
	Worst-case	1.34	0.5	2.68
		26.66	0.5	53.32
decarbonisation sludge	Best-case	0.91	0.5	1.82
	Worst-case	24.24	0.5	48.48



4.2 Cross-linked SAPs

Cross-linked SAPs are used directly as soil conditioners in order to increase soil water retention capacity, to promote a slow nutrient release from fertilizers or for both applications combined. These soil conditioners can be composed by both PAMs or PAAs. The environmental behaviour and fate have been shown to be similar for cross-linked compositions and linear PAMs. Once applied to the soil, these gels are purposely designed to be stable for several years and to not migrate. In fact, they also show strong adsorption to soil particles. The transfer to water is assumed to be even lower than for linear PAMs, because of the insolubility of the cross-linked structure. Although ecotoxicological data on aquatic organisms is almost inexistent, the risk of PA/PAA SAPs to water species can be considered to be low, because no relevant concentrations of gels are expected to be found in waters. However, as for linear PAMs, cross-linked PAMs/PAAs could release some potential toxic by-products during their degradation, which could leach into waters. A better knowledge on degradation products of SAP gels would be useful. As for linear PAMs, tests with SAPs on sediment organisms would provide additional information about their impact.

Concerning the soil compartment, it is difficult to estimate realistic exposure in the field. First, the models applied are not validated for polymers. In addition, most of SAP products are proprietary and their formulation is not available. For some products, the nature of the composing polymer is not available and often the proportion of the polymer in the formulation is not provided. Finally, hydrogels are mostly applied punctually, e.g. around the target plants. It is then important to consider that the derived PECs do not indicate a homogeneous concentration in the whole field but rather a punctual concentration, while the surrounding soil could be completely uncontaminated. The elaboration of a PEC model more adapted for cross-linked hydrogels, would be a useful instrument, to better evaluate their environmental exposure. Given the low application interval (e.g. several years), SAPs are less likely to accumulate compared to flocculants. On the other hand, their half-life is even higher than linear PAMs, which makes them highly persistent.

The PECs calculated are very variable, because of the reasons explained previously, and can often be limited to the target area. However, many them range from hundreds to thousands mg/kg. As a consequence, soil organisms may be exposed to very high concentrations for a long time. Despite that, ecotoxicological data of SAPs are also very rare. Studies on the effect on microorganisms and on plants are contrasting. Being biodegradable, these gels can often enhance some microorganism populations, because they can use them as food source, while other microbial species can either be not impacted or even negatively affected. Concerning plants, it seemed that when used according to the recommended instructions, plant growth can be promoted, while in other cases it can be inhibited. The formation of intermediary products toxic to plants has also been shown, confirming the need to better evaluate the effects of degradation of SAPs in the soil. A PNEC is not possible, due to the scarcity of ecotoxicological studies. The lowest effect values resulted from field studies for microorganisms (0.1 % d.w.) and woody plants (800 mg/kg). Although they do not allow a generalization for all plant and microorganisms, these thresholds were in the range, and in some cases lower, than the PECs derived in the present study. If assumed that PAM-based SAPs have a similar impact than linear PAMs, then RQ could be approximated, using the PNEC of 0.5 mg/kg derived for flocculants (see section 4.1). All SAPs containing PAM, as well as PAA, have PECs considerably higher than 0.5, resulting in a RQ always greater than 1. This would indicate a risk for terrestrial organisms, although the similarity between linear and cross-linked PAMs is just an assumption. As for linear PAMs, data gaps about ecotoxicological effect of cross-linked PAM/PAAs to soil organisms are existing, and bioassays on the most representative species would be a necessary step for conducting an appropriate risk assessment.

4.3 Regulation/comparison to other countries

Both linear and cross-linked polymers considered in the present report have been generally considered non-toxic for the environment (see 1.2. and 3). The only concern surrounding PAM



use has been mostly the possibility that they could be depolymerized into their original toxic monomers. The residual monomer content has to be maintained under legal values, which are defined by the concerned authority. For example, the European Union indicates a trigger value of 0.1 % (European Commission 2002a), while France suggests a limit of 500 μgkg^{-1} (Anses 2012b) and Italy proposes a maximal content of 0.05 % (Italian Republic 2010). Given the concern raised from AMD toxicity, when the topic of environmental safety is addressed, most studies tend to consider the degradation of the polymers, and considering the eventual release of toxic monomers, especially AMD. Although AMD release is commonly accepted to not occur under environmental conditions, some concern still exist and other degradation products are generally not considered. Besides degradation, exposure scenarios and effects to organisms, need to be evaluated, in order to establish a proper environmental risk assessment (European Commission 2003). However, this approach has been rarely used for polymers, which have generally been subjected to exemptions or reduced regulatory requirements in various countries (Deloitte 2014). For instance, in 2007 PAM was considered as a macropollutant with low toxicity and side effects (Sojka et al. 2007). More targeted regulations on synthetic polymers are often scarce and change depending on the country.

In France, certain polymeric products used in agriculture, including some water retention agents, are submitted to evaluation and decision for authorisation to the French Agency for Food, Environmental and Occupational Health & Safety (e.g. Anses 2012a), while for other polymers, only broad information concerning their biodegradability is provided. A recent evaluation of ANSES highlighted that the possibility of accumulation of persistent polymers, including PAMs, cannot be excluded by only defining the product as “biodegradable” and indicated the need of further studies, focusing on the impact and on the degradation behaviour of some polymers used in agriculture (Anses 2012c). The term “biodegradability” is globally used by manufacturers, especially for SAPs, to support the fact that a product is environmentally safe (communication from the manufacturers and information retrieved on technical information of the products). However, the specification “biodegradability” does not provide information about the half-life of the product in the soil and, as reported from ANSES, this control is not enough to guarantee that a product would not accumulate or would not be toxic.

An example, which took into consideration the half-life of polymers in the soil, is Germany. The German Fertilizer Ordinance (DüMV) introduced in 2012 a general precautionary measure, stating that all synthetic polymers entering the soil should not have a degradation rate below 20 % in a 2-year period (DüMV 2015). Also, the Ordinance regulates the use of SAPs, stating that if products contain synthetic polymers, then the amount of applied product must not exceed 150 kg of active substance (A.S.) / ha within 10 years of usage. The requirements do not apply to punctual applications (e.g. planting holes), for which a dose of 4 kg of synthetic polymers (A.I.) / m^3 of soil must not be exceeded. If considering the application rates reported in the section 2.2.2, these exceed the trigger values suggested in the DüMV for the products B, G, H and I (see Table 5).

Taking into consideration the degradation rate is helpful for assessing the safety of a polymer, but it is sometimes not enough if not all degradation products are considered (see e.g. ANSES, this report). In addition, while the environmental concern on synthetic polymers keeps focusing mostly only on their degradation behaviour, ecotoxicological bioassays are still not considered necessary, especially for SAPs. However, also linear PAM were first considered as environmentally inert but recent studies about their ecotoxicological effects have indicated their mechanical adverse effect on water organisms (see 3.1.1). Given the similarity in the composition between linear PAM and some cross-linked SAPs (especially PAM), the latter could cause as well a risk to soil species. More generally, a better understanding of the impact of synthetic polymers on organisms, belonging to all environmental compartments is thus required, in order to perform a complete risk assessment. Furthermore, the degradation behaviour needs to be assessed more specifically. The need for reviewing the REACH approach on polymers was indicated already in the REACH Regulation in Article 38(2), stating that the European Commission may present proposals for registering a range of selected polymers (REACH 2006). In this direction, some working groups have been focusing recently on strategies for classifying certain categories of



polymers and better define their evaluation and regulation (Deloitte 2014; ECETOC 2019). At the moment, the European Commission is actually seeking proposals for projects, aiming to identify and evaluate the categories of polymers which can be categorised as being of concern (Chemical Watch, 2019). The European regulation on polymers has only recently been modified in the new Regulation on Fertilizers (European Commission 2019) with entry into force in June 2019. The Regulation states that from now on, fertilizers are permitted to only contain polymers (except for nutrient polymers), if such polymers have the purpose of retaining water or promoting a controlled release of the fertilizer. In order to be permitted in fertilizers, these polymers are required (in the next seven years) to meet specific biodegradability criteria. Such criteria and the appropriate methods for testing will be defined by the Commission. This should ensure that the polymer used can be completely degraded in soil and water, meaning that at least 90 % of the organic carbon is converted into carbon dioxide, in max. 48 months after the claimed functionality period. The other ultimate degradation products shall be biomass and water. Also, the use of polymers should not lead to accumulation of plastics in the environment. In addition, the polymer and its degradation by-products will need to pass a plant growth acute toxicity test, an earthworm acute toxicity test and a nitrification inhibition test with soil microorganisms, in order to prove no adverse effects to the soil environment.



5 Conclusion

In the present study, two main categories of polymers were considered: linear PAM as contaminants in soil improvers and cross-linked SAPs as active ingredients of soil improvers. For both categories of substances, the main objectives of the present study were:

- 1) To make predictions about an exposure scenario in the environment
- 2) To summarize the actual knowledge about the ecotoxicological effects of such polymers
- 3) To compare exposure and effect, and derive critical limit values, where possible
- 4) To report and highlight the knowledge gaps and suggest strategies in order to fill them

The main conclusions are resumed in Table 8. Both linear PAMs and cross-linked SAPs are persistent and accumulate in the soil. Transfer to waters is less likely but if this is the case, products can reach the sediment compartment, too. For this reason, knowledge about their effect on soil, and eventually sediment organisms, is necessary, while data for the water compartment are less needed. There are few publications suggesting that PAMs and SAPs can pose a risk for some specific species of earthworms and plants. Since available information about the effect of PAMs/PAAAs to soil organisms is scarce, more terrestrial ecotoxicological bioassays are needed to better assess the risk of long-term exposure to such polymers at all trophic levels. Furthermore, the behaviour and environmental fate of some products released during the degradation of PAMs/PAAAs in soil needs to be better evaluated, for instance by field studies. The traditional Risk Assessment Evaluation proposes strategies for the evaluation of single substances, but methods for assessing the environmental risk of polymers are still limited, especially for the soil compartment. Given the lack of appropriate models, the values derived in the present report are to be taken only as an approximation. The high variety of existing polymers and products containing polymers pose an additional difficulty and the ecological risk assessment should consider each specific formulation and use. This work highlighted the growing need for new strategies for assessing the risk of polymers, and substances in general, to soil organisms. The recent European Regulation has already made progress in this direction, with stricter requirements for polymers in fertilizers. However, the current low number of available bioassays and the development of a respective risk assessment will be a great challenge for the whole field of ecotoxicology.



Table 8: Exposure, effect, risk, and data gaps derived in the present study, for the two categories of polymers (linear PAMs and cross-linked SAPs) and their use

	Linear PAM			Cross-linked SAP		
	Exposure	Effect	Data gaps	Exposure	Effect	Data gaps
Soil	Persistent with risk of accumulation. Worst-case: PEC = 26.66 mg/kg (gravel sludge) Best-case: PEC = 0.10 mg/kg (gravel sludge)	PNEC = 0.5 mg/kg (<i>E. fetida</i> , reproduction)	Ecotoxicological bioassays at all trophic levels. Field assays on PAM degradation.	Worst case: PEC = 1915 mg/kg (extended application) or 9183 (punctual application) Best case: PEC = 3 mg/kg (extended application) or 67 mg/kg (extended application)	No data. Few site-specific adverse effects at 800 mg/kg	Ecotoxicological bioassays at all trophic levels. Field assays on PAM degradation.
	RQ = 0.2 to 53.32 Possible risk			RQ cannot be calculated		
Water	Low transfer PEC cannot be calculated	PNEC = 0.05 mg/kg (<i>D. magna</i> , growth)	Field assays on PAM degradation.	Very low transfer, PEC cannot be calculated	No data	Field assays on PAM degradation.
	RQ cannot be calculated Low risk, but possible risk to degradation products			RQ cannot be calculated Low risk, but possible risk to degradation products		



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7 Glossary

AA	Acrylic Acid
AMD	Acrylamide
EC50	Effect concentration leading to half of the response
EC10	Effect concentration leading to 10 % of the response
ECHA	European Chemicals Agency
EMA	European Medicines Agency
FOAG	Federal Office of the Agriculture
FOCUS	FORum for the Co-ordination of pesticide fate models and their Use
LOEC	Lowest Observed Effect Concentration
MEC	Measured Environmental Concentration
NOEC	No Observed Effect Concentration
PAM	Homo-polymer or co-polymer containing AMD monomer unit
PAA	Homo-polymer or co-polymer containing AA monomer unit and/or related monomers
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
SAP	Super Absorbent Polymer



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Appendix 1 SAP application rates

Some application rates of SAPs, reviewed by Sanz-Gomez et al. (2015)

Application rate (kg/ha)	Reference
1000	Kazanskii and Dubrovskii,
3000	1992
20	BASF trials, Sanz-Gomez,
30	2015
10	Mao et al., 2011
15	
20	Ashkiani et al., 2013
40	
5	
15	Islam et al., 2011
60	
30	
5	Narjary and Aggarwal, 2014



Appendix 2 Aquatic toxicity data for linear PAMs

See Excel dossier.