Water-soluble and Water-dispersible Polymers Used in Commercial Agricultural Formulations: Inventory of Polymers and Perspective on their Environmental Fate

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Abstract: Agricultural formulations contain water-soluble and water-dispersible polymers (WSPs and WDPs) to increase the application efficiency of the active ingredients (*e.g.* pesticides and fertilizers). Despite their direct release to soils and crops, there is currently no inventory of used polymers and their fate in soils is poorly studied and understood. Herein, we identify WSPs and WDPs used in agricultural formulations on the German and Swiss markets. By searching the scientific literature, patents, and manufacturer websites, we tentatively identified that 233 of the 1815 listed trade names of formulation additives contained polymers, the majority of which belonged to three main chemical classes: polyethylene glycol (PEG)-based (co)polymers, functionalized polysaccharides (PSacs), and vinylic (co)polymers (VCPs). We report information on their functionalization, molecular weights, and market significance. In 2015, their estimated combined annual application volume in Switzerland surpassed 100 tonnes. Low molecular weight PEGs and natural, unfunctionalized PSacs reportedly biodegrade, suggesting no accumulation in soils associated with their use as formulation additives. Conversely, high molecular weight functionalized PEGs, functionalized PSacs, and the majority of the VCPs have been reported to undergo only slow or no soil biodegradation. These polymers may thus persist and accumulate in agricultural soils, requiring more detailed investigations of their environmental fate and resulting exposure scenarios. There is a need for systematic studies on the effects of polymer structure, molecular weight, and functionalization on soil biodegradability.

Keywords: Agricultural additives · Biodegradation · Environmental fate · Water-dispersible polymers (WDPs) · Water-soluble polymers (WSPs)

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1. Introduction

Modern agriculture faces the challenge of ensuring a stable food supply for a growing global population, while contending with the effects of climate change and associated freshwater scarcity.[1] A key strategy to address this challenge is the adoption of novel technologies that increase crop yields and, at the same time, aim at minimizing the environmental impact of food production. One such technology is the use of synthetic polymers in agricultural production. The benefits and potential risks associated with the use of agricultural plastics (*i.e.* materials made from structural, non-soluble polymers) are currently subject to extensive research.[2–5] By comparison, water-soluble polymers (WSPs) and water-dispersible polymers (WDPs) have received much less attention. However, these polymers are a major component of agricultural formulations applied to crops and soils. The active ingredients in these formulations, including insecticides, herbicides, fungicides, and/or fertilizers, serve to increase crop health by combating pests and optimizing nutrient supply. WSPs and WDPs in the formulations stabilize the active ingredients, prevent their evaporative losses, and reduce their wash-off after application.[6–8] As a result, WSPs and WDPs lower the required

amounts of the active ingredients and, thereby, improve the application efficiency of many pesticides and fertilizers (or even enable the use of specific compounds in the first place).

Over the past decades, substantial research has been directed towards understanding the environmental chemistry and ecotoxicological impacts of the active ingredients in agricultural formulations. In contrast, the environmental chemistry and fate processes of WSPs and WDPs from these formulations remain very poorly studied and understood. Furthermore, potential impacts of WSPs and WDPs on soil health and soil ecosystem services remain poorly studied. The resulting knowledge gaps call for research on the environmental chemistry and potential impacts of WSPs and WDPs used in agricultural formulations. As for low molecular weight (*i.e.* non-polymeric) organic chemicals, the fate of WSPs and WDPs in agricultural soils is controlled by transfer and transformation processes. These processes depend on the backbone chemistry, the charge and the molecular weight of the polymers.[9] Transfer processes include adsorption to soil particle surfaces as well as vertical and horizontal transport of the polymers through the soil. Adsorption of WSPs and WDPs to soil particle surfaces decreases their mobility and bioavailability. Transfer processes have in common that they do not alter the chemical structure of the WSPs and WDPs. Conversely, transformation processes involve abiotic or enzymatically mediated reactions that change the chemical structure of the WSPs and WDPs.

Knowledge gaps on the fate of WSPs and WDPs in soils call for careful evaluation of which polymers are used. In particular, the use of WSPs and WDPs that are stable, and thus have the potential to accumulate, needs critical evaluation. More research is warranted to allow developing exposure scenarios which are required as part of the environmental risk assessment of WSPs and WDPs.

Authorities have also recognized the need for information on environmental transfer and transformation processes of WSPs and WDPs, including data on their (bio)degradation and adsorption to soil or sediment.[10–12] The European Chemicals Agency (ECHA) initially viewed water-soluble and water-insoluble polymers as being of low(er) environmental concern, resulting in the exclusion of the polymers from the 'European Registration, Evaluation, Authorisation and Restriction of Chemicals' (REACH) system when it was introduced.[13] This exemption has been under review since 2012. More recent reports by the European Commission, evaluating registration requirements under REACH, proposed to distinguish between polymers of low concern (PLCs) and polymers requiring registration (PRRs).[10–12] Central to this distinction is information on the environmental fate and potential effects,[10–12] which depend on the structure, molecular weight, charge, number of reactive functional groups and surface-active properties of the WSPs and WDPs.

The regulatory attention to WSPs and WDPs is aligned with an increasing interest of the scientific community on the environmental fate of these polymers, as evidenced from a recent increase in the number of viewpoints, perspectives and reviews published on this topic.[6,8,9,14–18] These publications highlight advancements in the developments and challenges in assessing the environmental fate of WSPs and WDPs.

As alluded to above, transfer and transformation processes of WSPs and WDPs, along with potential effects, are primarily determined by the chemical structure and molecular weight of these polymers. Therefore, a critical first step in assessing the fate of WSPs and WDPs in soils is to provide a structure-based inventory of commonly used polymer structures in agricultural formulations. There is currently no such inventory in the scientific literature.

This perspective article has two main objectives. The first is to provide an inventory and a classification of WSP and WDP chemical structures used in agricultural formulations and estimate their market shares. To this end, we analyzed available data for the agricultural formulation markets in Germany and Switzerland. The second objective is to provide an assessment of the transfer and transformation processes occurring in soils for polymers within the dominant classes of identified WSPs and WDPs. This assessment draws both from the limited published data on fate processes of WSPs and WDPs in soil and the knowledge on adsorption of WSPs to isolated and well-characterized minerals. The discussion of the WSP and WDP fate will highlight potential benefits of using soil-biodegradable over stable (persistent) polymers in agricultural formulations.

2. Methodological Approach

2.1 *Method for Identification and Classification of WSP and WDP Chemical Structures*

We based our analysis on the trade names of additives used in agricultural formulations listed in the document 'Beistoffe in zugelassenen Pflanzenschutzmitteln' ('Additives in authorized crop protection products') published by the German Federal Office of Consumer Protection and Food Safety on November 1, 2020.[19] We hereafter refer to this document as *BzP2020*. The *BzP2020* lists a total of 1,815 trade names in authorized agricultural formulations in alphabetical order. A single trade name in this list refers either to a single chemical additive or to several additives (*i.e.* an additive mixture). For each listed additive trade name, we assessed if it referred directly to a polymer or to a mixture of additives if the mixture contained a polymer. For this purpose, we defined 'polymer' conservatively as a 'macromolecule' with at least five repeating units. We subsequently classified each identified polymer by its backbone structure, counting each structure as a 'hit'. We then used the information available through the search (see below) to compile a molecular weight range of the identified polymers within each polymer class.

To procure this data, we employed a three-step search procedure, using the trade name of the additive as the search keyword: (i) We started with a *Google Scholar* search. Whenever available, we relied on peer-reviewed literature to obtain information. (ii) If the search on *Google Scholar* yielded insufficient information for a given trade name, we continued the search using *Google Patents* and looked for information on the composition in public patents. (iii) In cases that also the *Google Pate*nts search provided insufficient information, we expanded our search to the *Google* search engine, targeting websites of suppliers and distributors. In very few cases, this three-step search procedure did not provide sufficient information. We then directly reached out to the respective companies or suppliers of the polymer (specifically to Mitsubishi Chemicals Europe, Kuraray Europe GmbH and Celanese).

We estimated the economic relevance of the different WSPs and WDPs in Switzerland based on the document 'Beistoffe in Pflanzenschutzmitteln – Vorstudie' ('Additives in crop protection products – preliminary study') published by the Federal Food Safety and Veterinarian Office in Switzerland in 2018.[20] This study, hereafter referred to as document *BPV2018*, identified the five top-selling formulation types used on the Swiss agricultural market based on sales data from 2015. For each of the five formulation types, an 'average' formulation composition was derived from a detailed analysis of the additives in ten representative products selected. By multiplying the sales data for each formulation type by its respective average composition, the study provided a list of additives ranked by their estimated quantity used.

Our analysis of chemical identities and market volumes of WSPs and WDPs is constrained to Germany and Switzerland based on the documents *BzP2020*[19] and *BPV2018*[20] referring to additives in crop protection formulations approved for use in these two countries. However, we presume that our findings are transferable to other countries: most formulations are produced and

distributed by internationally operating companies, which likely market similar, if not identical, formulations across the European market and possibly beyond.

2.2 Method for Assessing the Environmental Fate of Identified WSPs and WDPs

We assessed transfer and transformation processes in agricultural soil for the polymers in the identified major polymer classes based on the scientific literature. For transfer processes, we focused on studies on WSP and WDP adsorption. Given that there are only few studies on adsorption in soils, we also included adsorption studies to model mineral surfaces (such as clay or silica) in our analysis. For transformation processes, we primarily aimed at assessing if the polymers undergo biodegradation in soils. To this end, we searched for studies assessing the biodegradability of the identified polymers in (agricultural) soils. We focused on studies that evaluate biodegradability through mineralization of the polymer carbon to CO_2 and excluded studies that use inconclusive measurement endpoints, such as the gravimetric weight loss of added polymer. In cases that no soil biodegradability data was available, we screened the literature for studies reporting breakdown of the polymers by microbial extracellular enzymes. While enzymatic breakdown does not prove biodegradability, it often constitutes the critical first step in this process, producing breakdown products that are sufficiently small for microbial cell uptake and subsequent intracellular metabolic utilization.

3. Identification and Classification of WSP and WDP Chemical Structures

A comprehensive list of all additive trade names identified as polymers, their molecular weights (MWs; if available) and the re-spective references from which the information was obtained (i.e. either peer-reviewed papers, patents, or websites) are provided in Tables 1–5 in the Supplementary Information (SI). According to our analysis, around 13% (i.e. 233 hits) out of the total of 1,815 trade names listed in ref BzP2020[19] either referred directly to a polymer or to additive mixtures that contained a polymer. The following polymers were identified in the order of decreasing number occurrence (i.e. from highest to lowest number of hits): PEGs > polypropylene glycols (PPGs) > polysaccharide, non-functionalized and functionalized (PSacs) > polyvinyl alcohols (PVOHs) > polyvinyl acetates (PVAcs) > acrylic > polyvinyl pyrrolidones (PVPs) > polystyrenes (PSs) > others. The general structural formulas for these polymers are provided in Fig. 1a. We grouped these polymers in four major classes: polyethylene oxides (PEOs), polysaccharides (PSacs), vinylic (co)polymers (VCPs, including homopolymers and copolymers), and others (Fig. 1a, b). The number abundance of each polymer class is shown in Fig. 1b (with the number of hits provided in parentheses). The predominant WSPs and WDPs are PEG-based (ca. 52% of all polymers). This group is followed by vinylic polymers (VCPs, ca. 29%) and PSacs (ca. 15%).

Polyethylene glycols (PEGs). All trade names, molecular weights, and corresponding references related to PEG-based WSPs and WDPs are provided in Tables 1–3, SI. We also reported on the role of a given PEG in the respective formulation in cases that this information was provided in the reference(s).

Unfunctionalized PEGs constitute a smaller subset (ca. 13% (= 16/122) of PEGs). PEGs in which the hydroxy end groups are functionalized occur more prevalently (ca. 50% (= 61/122) of PEGs). PEG end groups were predominantly functionalized with castor oil and C4 to C18 alcohols. Another important subgroup
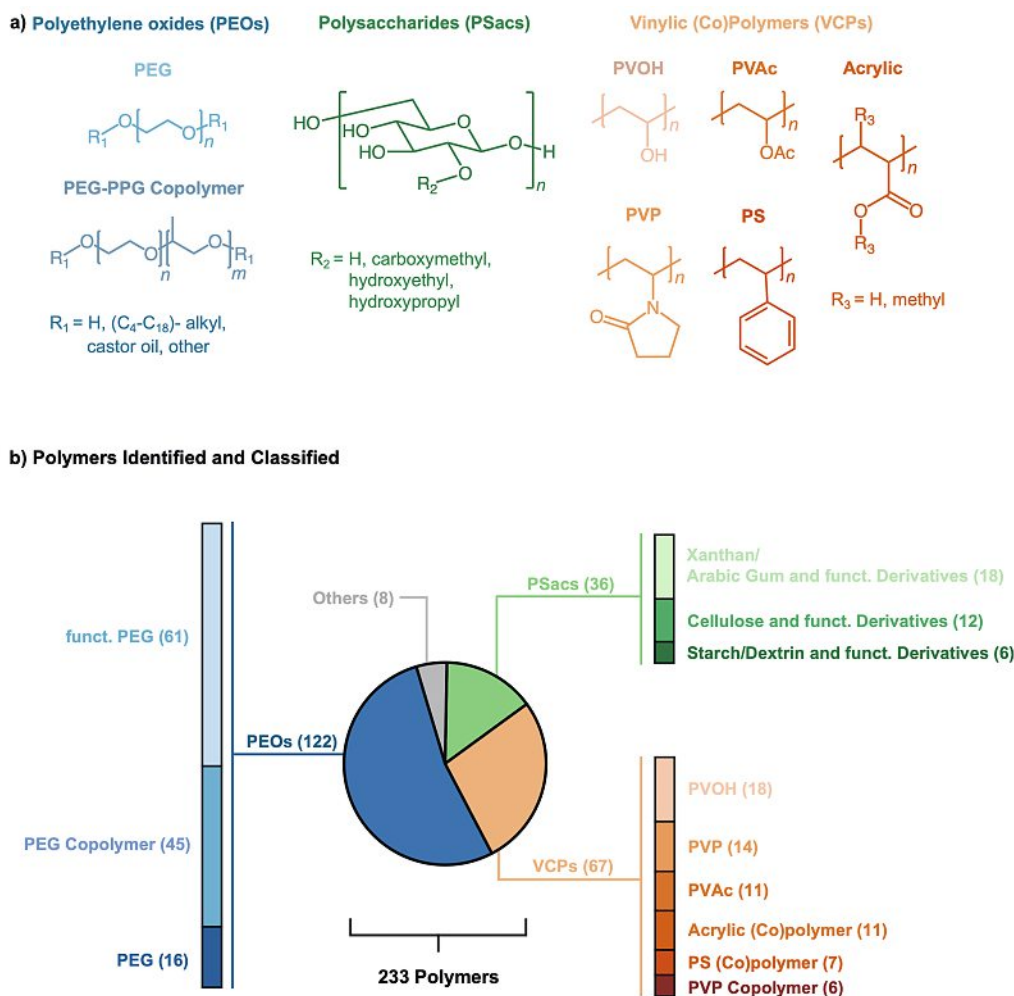

Fig. 1. a) Structures of polymers identified in research articles, patents and on websites when searching for the trade names of the additives listed in the document 'Beistoffe in zugelassenen Pflanzenschutzmitteln' (*BzP2020*).[19] b) Absolute occurrence (identified hits) of polymers in the additive list (i.e. a total of 233 polymers were identified in the list of a total of 1815 trade names). The major polymer classes were polyethylene oxides (PEOs, blue colors, including non-functionalized and functionalized (abbreviated 'funct.') polyethylene glycol (PEGs) and polypropylene glycol (PPGs)), polysaccharides (PSacs, green colors) and vinylic (co)polymers (VCPs; orange-red colors; including polyvinyl alcohol (PVOH), polyvinyl acetate (PVAc), acrylic, polyvinyl pyrrolidone (PVP) and polystyrene (PS) scaffolds). The corresponding trade names and references can be found in Tables 1–5 in the Supplementary Information (SI).

are PEG-copolymers (*ca.* 37 % (= 45/122) of PEGs), typically in conjunction with polypropylene glycol (PPG). For many of these polymers, the search provided information on the MWs (note that the MWs reported refer to the structures of the polymer, without accounting for the additional MW from end-group functionalization). While unfunctionalized PEG (co)polymers have MWs as high as 17'000 Da, the reported MWs of most functionalized PEGs are lower and range between 200 and 3'000 Da (Fig. 2a). The function of the PEGs in the formulations seems tied to their MWs: functionalized and non-functionalized PEGs with lower MWs are predominantly employed as non-ionic surfactants, whereas PEGs with higher MWs act as thickeners, dispersants, or emulsifiers.

Vinylic (co)Polymers (VCPs). All trade names that link to VCPs, their MWs and corresponding references are provided in Table 4, SI. The references also provide information on the role of the VCPs in the formulation.

Among the VCPs, PVOH make up the largest subgroup (*ca.* 27% (= 18/67)) followed by PVP (*ca.* 21% (= 14/67)), PVAc (*ca.* 16% (= 11/67)), acrylic (co)polymers (*ca.* 16% (= 11/67)), PS (co)polymers (*ca.* 10% (= 7/67)) and PVP copolymers (*ca.* 9% (= 6/67)). The acrylic (co)polymers are usually composed of monomers of acrylic acid, methacrylic acid or methyl methacrylate. PS is often copolymerized with acrylic polymers (and categorized herein as PS copolymers), while PVP is often copolymerized with PVAc (and categorized herein as PVP copolymers). The reported MWs of PVOHs and PVP range from *ca.* 6'000 to around 400'000 Da and from 10'500 up to 1'700'000 Da, respectively (Fig. 2b).

The search results suggest that PVOHs and PVACs in the formulations primarily serve to enhance the adhesion and film-forming properties of the formulations. PVP seems to be predominantly used as a thickening agent or emulsifier. Acrylic copolymers appear to mainly act as surfactants, dispersants, or emulsifiers. However, the actual purpose for the addition may vary based on the specific application.

Polysaccharides (PSacs). The third largest polymer class contain PSacs, representing approximately 15% (= 36/233) of the total identified polymers. All search information is compiled in Table 4, SI. The search provided MW information only for four functionalized PSacs used as agricultural additives which range from 95'000 to 1'000'000 Da (Fig. 2c).

Among the PSacs, xanthan gum and arabic gum are the subcategories with largest number of hits (*i.e.* 50% (= 18/36) of the PSacs). These are followed by functionalized and non-functionalized cellulose (representing *ca.* 33% (= 12/36) of the PSacs), and by functionalized and non-functionalized starches and dextrins, accounting combined for approximately 17% (= 6/36) of the PSacs. Due to the limited information on the MWs for the PSacs used as additives in agricultural formulations, we complemented our assessment with general literature data on naturally occurring PSacs: Xanthan gum and starches are examples of branched PSacs, and their average MWs can span from 100'000 to 80'000'000 Da.[21,22] Gum arabic, a natural composite PSac, comprises highly branched chains and their MWs range between 300'000 to 1'000'000 Da.[23] Natural cellulose, which is an unbranched PSac, typically has MWs that range from 27'000 to 900'000 Da.[24] Contrastingly, dextrins have the lowest MWs and range from 800 to 70'000 Da.[25] PSacs, both functionalized and non-functionalized, primarily serve as binders, thickeners, stabilizers or emulsifiers in agricultural formulations.

4. Economic Market Share of WSPs and WDPs in Switzerland

We used the list of additives from the *BPV2018*[20] document and, applying the search method detailed in the section above, identified which additives were or contained polymers. We then allocated these polymers to the polymer classes mentioned in the previous section. Fig. 3 illustrates the estimated cumulative sales volume for each polymer class for 2015 on the Swiss agricultural formulation market. PEG and PPG-based polymers (MWs unknown) dominated, with an estimated annual sales volume of *ca.* 95 tonnes/year. The most common end-group functionalizations were castor oil, C9–18 alcohols and tristyrylphenol, in good agreement with the predominant structures identified based on the German list of additives *BzP2020*[19] (see Fig. 1b). The second largest WSP and WDP subgroup in terms of annual sales was
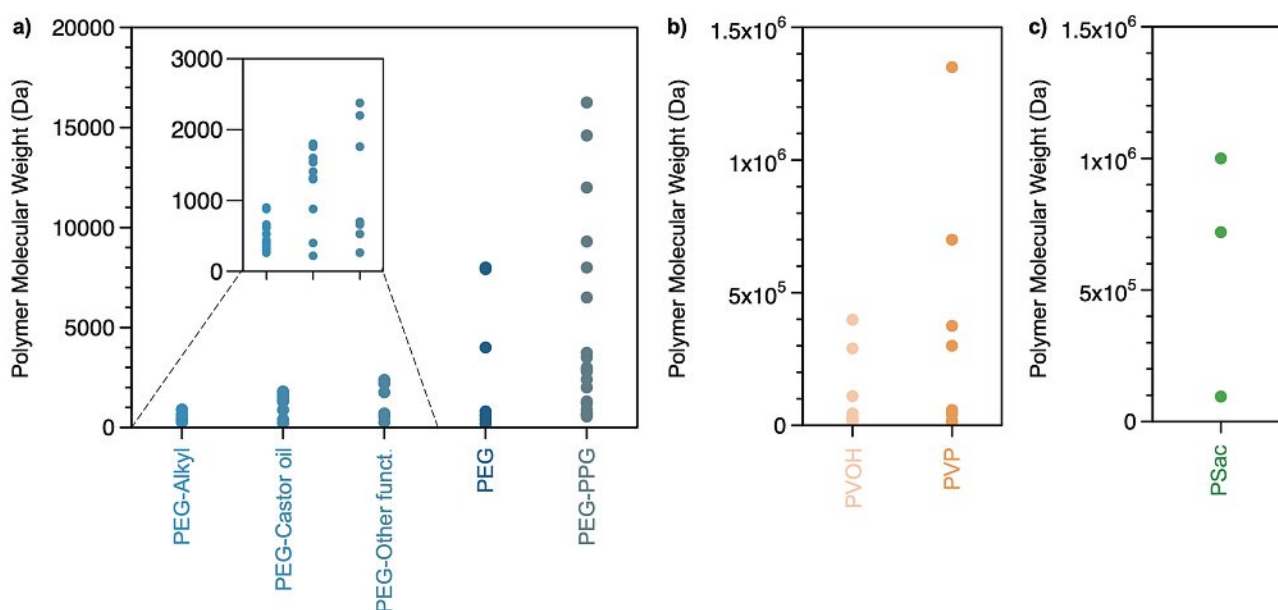

Fig. 2. Literature information on the molecular weight (MW) ranges of a) polyethylene glycols (PEGs, blue symbols) homopolymers, copolymers with polypropylene glycols (PPGs, blue symbols) as well as PEGs with different end group functionalization, and b) of polyvinyl alcohols (PVOHs, orange symbols) as well as polyvinyl pyrrolidones (PVPs, orange symbols), and c) polysaccharides (PSacs, green symbols), all identified as polymer additives in the document 'Beistoffe in zugelassenen Pflanzenschutzmitteln' (*BzP2020*).[19] The information on molecular weights as well as the corresponding sources for this information are provided in Tables 1–5 in the Supplementary Information (SI).

PSacs, which include both functionalized and unfunctionalized polysaccharides, with *ca.* 4.5 tonnes/year. Among the functionalized PSacs, the sugar OH- group was most commonly derivatized by a hydroxyethyl group. VCPs – including acrylic copolymers, PVOH, and PVP – had an estimated sales volume of *ca.* 3.8 tonnes/year, similar to urea-formaldehyde polymers with a volume of *ca.* 3.7 tonnes/year. The urea-formaldehyde polymers were not as prominent in the *BzP2020*[20] document analyzed above, possibly because these polymers can serve as slow-release fertilizers and thus may have been considered an active ingredient rather than an additive.[26] The total amount of WSPs and WDPs used in agricultural formulations in Switzerland in 2015 thus amounted to an estimated 107.75 tonnes.

It is possible to provide a back-of-the envelope calculation for the amounts of WSP and WDPs applied per ha of agricultural land. According to the land use statistics published by the Swiss Federal statistical office in 2018, a total of 3,884 km^2 were used as arable land in Switzerland.[27] We here make the simplifying assumption that all agricultural formulations sold in Switzerland were also used and that they were evenly applied to the above area of arable land. This assumption implies that we underestimate the actual polymer inputs on fields that receive more intensive applications of formulations. Also, we do not account for weather-dependent variations in the applied amounts of formulations nor for applications in response to specific incidences (*i.e.* in response to a pest infestation). Based on the data in the *BPV2018*[20] document, an estimated 3'640 tonnes of agricultural formulations were sold in Switzerland. This corresponds to an annual application of approximately 9.5 kg of agricultural formulation or an estimated 300 g of WSP and WDP per hectare of arable land (about 30 mg/m^2).
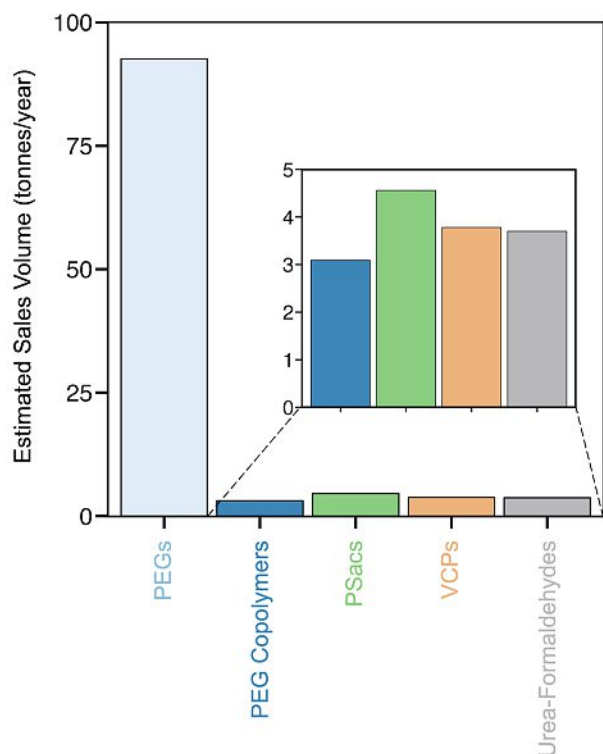

Fig. 3. Estimated annual sales volume of water-soluble and water-dispersible polymers used in agricultural formulations for the larger classes of polyethylene glycols (PEGs), PEG copolymers, polysaccharides (PSacs), vinylic (co)polymers (VCPs) and urea-formaldehyde polymers in Switzerland, based on market data from 2015. These classes here contain both non-functionalized and functionalized polymers. The data is derived from the document 'Beistoffe in Pflanzenschutzmitteln – Vorstudie'[20] (*BPV2018*).

5. Assessment of the Environmental Fate of Identified WSPs and WDPs

Transfer processes. The adsorption of charged WSPs is expected to be dominated by electrostatic interactions – which either are attractive or repulsive – with charged soil particle surfaces.[28] Negatively-charged polymers (*e.g.* carboxymethyl cellulose) are expected to strongly adsorb to positively charged iron- and aluminum (oxyhydr-)oxide surfaces as well as to the edge sites of clay minerals but be electrostatically repelled from negatively charged surfaces, such as found on silica and soil organic matter surfaces.[28] The opposite trends are expected for positively charged polymers. By comparison, the adsorption of non-charged WSPs (*e.g.* PEGs) is dependent on their capability to form hydrogen bonds with H-accepting and -donating functional groups on soil particle surfaces.[28] In addition to the enthalpic contributions from electrostatic interactions and H-bonding, adsorption is entropically favored due to the displacement of surface-coordinated molecules or ions into solution upon polymer adsorption.[29,30]

In contrast to low molecular weight organic compounds that may diffuse in and out of micropores of soil particles as well as into soil organic matter, WSPs and WDPs are expected to mainly adsorb to soil particle surfaces. Adsorption results in the formation of multiple contact points between adsorbed polymer molecules and particle surfaces. Adsorption of polymer molecules therefore is often found to be irreversible, reflecting that desorption would require simultaneous detachment of the polymer molecule at all contact points from the surface.[28] WSPs and WDPs that experience strong adsorption to soil particle surfaces are expected to show low mobility in soils whereas polymers with weak adsorption to surfaces may show enhanced mobility and be transported from the topsoil to deeper soil horizons (Fig. 4).

Transformation processes. Transformation reactions can be both abiotic and enzymatically mediated (*e.g.* an abiotic or enzymatic hydrolysis of glycosidic bonds in the backbone of a PSac). For the assessment of WSP and WDP stability, reactions that cleave their backbone are particularly relevant as they result in smaller molecules and hence facilitate uptake into microbial cells, thereby enabling biodegradation – arguably the most substantial transformation reaction of WSPs and WDPs in soils. Biodegradation describes the process in which microbes convert all polymer carbon into CO_2 (and possibly also CH_4 under anoxic conditions) and microbial biomass. As for biodegradable structural polymers (and plastics), biodegradation of WSPs and WDPs is a two-step process: The first step is the extracellular cleavage of the polymer backbone, which either involves abiotic reactions or is mediated by extracellular enzymes. Enzymatic cleavage may occur both at the terminal (end) groups (*i.e.* exolytic cleavage) or within the polymer chain (*i.e.* endolytic cleavage), depending on the enzyme specificity. The breakdown products need to be of sufficiently low molecular weight to be assimilable by microbial cells. While the maximum molecular weight for a compound to be taken up probably depends on its chemistry, it is likely to be in the range of 800 to max. 2'000 Da.[31] The second step of biodegradation, following cellular uptake, is the intracellular metabolic utilization of the breakdown products to generate energy under formation of CO_2 (and CH_4), a pathway referred to as mineralization, and the formation of microbial biomass.

Transfer and transformation processes of WSPs and WDPs in agricultural soils are interlinked: previous studies have shown that the adsorption of nucleic acids and proteins to soil particle surfaces hampers their availability for enzymatic breakdown in the soil pore-water.[32–34] At the same time, adsorption of WSPs and WDPs may retain them in topsoils characterized by higher microbial activity and hence probability for biodegradation.[35,36]

Polyethylene glycols. The hydrogen-bond accepting ether groups in the PEG backbone allow for PEG adsorption through H-bonding with acidic hydroxyl groups on mineral surfaces in
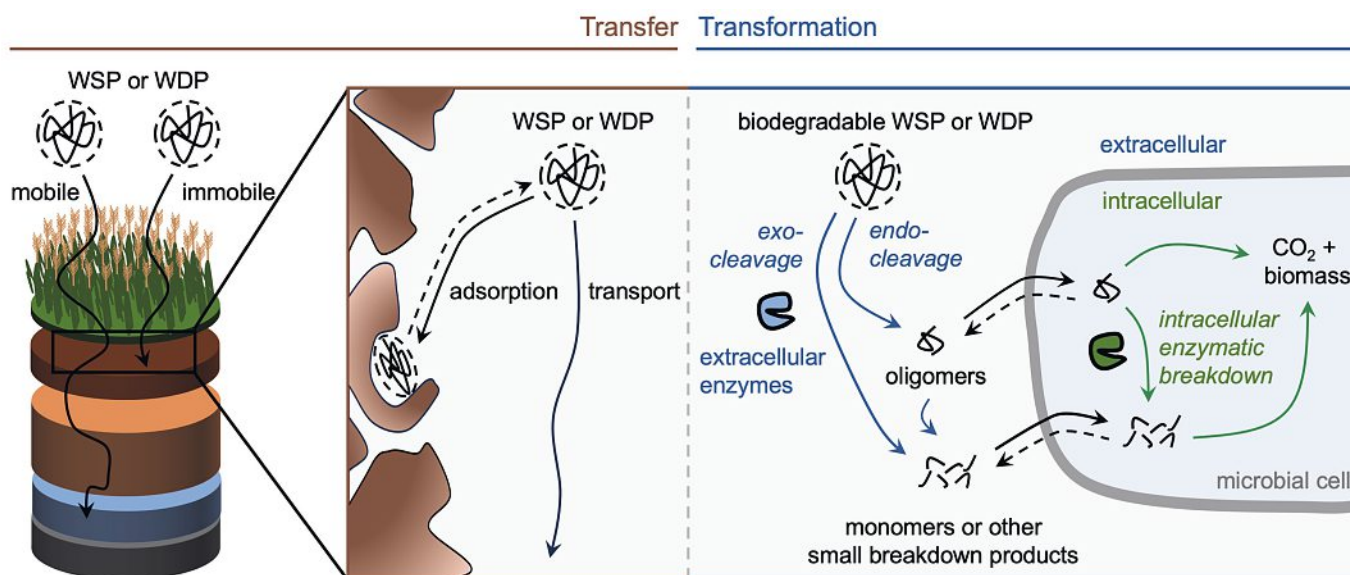
Fig. 4. Major anticipated fate processes of water-soluble polymers (WSPs) and water-dispersible polymers (WDPs) in soil. The fate processes can be divided into transfer (*i.e.* adsorption and transport) and transformation processes (*i.e.* extracellular enzymatic and abiotic breakdown as well as microbial utilization of breakdown products).

soils.[37] Given that PEG is uncharged, electrostatics do not contribute to its adsorption.[37] Reported adsorption capacities of PEGs on minerals such as silica or clay[37,38] are lower than those reported for charged polymers with strong electrostatic attraction to charged mineral surfaces. These findings suggest that PEG adsorption is comparatively weak, presumably due to competition with water molecules for H-bond donating sites in combination with the low polarity of the ether bond. Consistently, PEG with a molecular weight of 4'000 Da showed low adsorption and high mobility in sandy soils.[39]

PEGs and other polyethers do not have natural biopolymer analogues. Therefore, there are no soil enzymes reported that endolytically cleave the ether bonds in the PEG backbone. Furthermore, the ether bonds cannot undergo abiotic hydrolysis. Consequently, PEGs primarily degrade intracellularly through exolytic oxidation in aerobic systems,[40] a reaction cascade that involves three enzymes: an alcohol dehydrogenase and an aldehyde dehydrogenase – which convert the terminal alcohol groups of PEG into aldehyde and then carboxylic acid groups, respectively, and a third enzyme targeting the carboxylic acid end group, resulting in the release of glyoxylate from the PEG chain (Fig. 5a). Microbes that utilize PEG obtain energy from its oxidation and can also use the resulting glyoxylate as a carbon source for biomass formation.[41]

Soil microorganisms were reported to break down PEGs of varying sizes with MWs up to 20'000 Da.[42] However, there are only a few studies on PEG breakdown in soils. Slow biodegradation of ^{14}C-labelled PEG (4'000 Da) was reported for three typical tropical soils[43] (*i.e.* mineralization of 50% of PEG to CO_2 in 735 days). Another study conducted on low molecular weight PEG (400 Da) reported biodegradation within 42–71 days in agricultural topsoil.[44] These contrasting dynamics of the two PEGs suggest that biodegradation rates strongly decrease with increasing MW of the PEG. This observation suggests that the extracellular breakdown of large PEGs in soil pore water constrains the overall biodegradation rate. Consistently, low microbial uptake rates have been reported for PEGs with a MW greater than 2'000 Da.[31] Beyond the effect of molecular weight, functionalization or copolymerization of PEGs may hinder their biodegradability in soils. This hypothesis is supported by the decreased biodegradation rates of end-group functionalized PEGs in comparison to unfunctionalized analogues when exposed to various bacterial isolates from river water.[45]

Polysaccharides. Adsorption of uncharged PSacs in soils is expected to be governed by strong H-bond formation between the hydroxyl groups in their structure and respective H-bond donating and accepting sites on soil particle surfaces. As a result, uncharged PSacs exhibit adsorption capacities on silica and clay minerals that are notably higher than those of PEGs.[46–48] Charged PSacs interact with mineral surfaces mainly through attractive or repulsive electrostatics.[28] Consequently, electrostatic interactions with mineral surfaces also control the mobility of charged PSacs in soils.[28] In sandy soils, negatively charged PSacs exhibit enhanced mobility,[49] consistent with electrostatic repulsion from negatively charged silica surfaces.

Biodegradation of PSacs in soils involves hydrolytic cleavage of the glycosidic bonds in the PSac backbone to form mono- and oligosaccharides, followed by their uptake into microbial cells and intracellular metabolic utilization (Fig. 5b).[50–52] The soil-biodegradability of xanthan gum and guar gum is not well-documented in the literature. However, cellulose, starch, and dextrins are known to readily biodegrade in agricultural soils.[53–55]

There are no systematic studies on the effect of hydroxyl group functionalization on the biodegradability of PSacs in soils. However, biodegradability tests of carboxymethyl-cellulose in compost indicate that the functionalization slows down biodegradation.[56] Consistently, the enzymatic hydrolysis of the glycosidic bonds is hindered by hydroxyl group derivitization by methyl, hydroxyethyl or carboxymethyl groups.[57–59]

Vinylic polymers. Considering the extensive structural diversity of the vinylic polymers classified, our subsequent examination of adsorption will focus on PVOHs and PVPs.

PVOH is capable of both H-bond donor and acceptor interactions, while PVPs are strong H-bond acceptors. On silica surfaces and clay minerals, both PVOH and PVP show adsorption capacities that are in a range comparable to PSacs.[60–64] As a result, we anticipate low mobility of these polymers in agricultural soils.

The C–C backbone in VCPs is a highly stable molecular structure which cannot be readily cleaved, leading to low or non-measurable mineralization rates of VCPs in soils. Acrylic (co)polymers (crosslinked PAA) displayed <1% mineralization of its carbon atoms to CO_2 after six months in agricultural soils.[65] Notably, solid PS exhibited no significant biodegradation in soil over a period of 32 years, demonstrating its persistence.[66] However, partially hydrolyzed PVAc/PVOH have been reported to biodegrade,
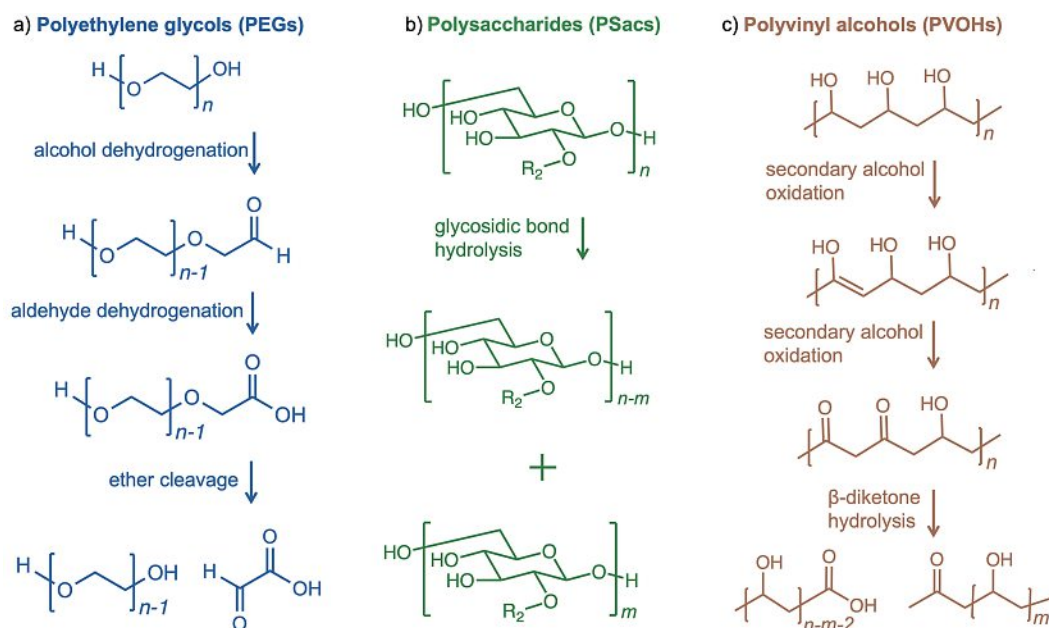
Fig. 5. Proposed biodegradation pathways of polyethylene glycols (PEGs), polysaccharides (PSacs) and polyvinyl alcohols (PVOHs).

likely involving random oxidative endocleavage of the polymer chains (Fig. 5c).[67] The first step in this process is the oxidation of the secondary alcohol group catalyzed by oxidase and dehydrogenase enzymes, resulting in the formation of β-hydroxyketone and 1,3-diketone structures. These 1,3-diketone groups then enable the cleavage of the carbon-carbon bond, driven by a specific β-diketone hydrolase, leading to the formation of carboxyl and 2-propanone end groups.[68] PVAc/PVOH with high (99 mol%) and very low (11 mol%) hydrolysis extents did not mineralize in soils while PVAc with hydrolysis extents between 24–73 mol% showed 50–60 % mineralization in soil over 720 days of incubation.[68] For testing of biodegradation, it is important to consider that the water solubility undergoes changes upon hydrolysis of PVAc/PVOH, with PVAc becoming water soluble at hydrolysis extents above approximately 75 mol%. We note that many of the PVOHs found in the *BzP2020*[19] list had hydrolysis extents above 90 mol%, suggesting that they biodegrade in soils only very slowly or not at all.

6. Conclusion & Outlook

Our analysis shows that WSPs and WDPs are common additives in agricultural formulations, with PEGs as the dominant polymer class, followed by PSacs and VCPs. In Switzerland, approximately 100 tonnes of these polymers were sold and applied to agricultural soils based on market data from 2015. Though more recent data is lacking, an uptrend in application amounts since 2015 is expected, mirroring the general surge in agricultural polymer use.

The environmental fate of the herein identified WSPs and WDPs in soils remains poorly understood. Among the polymers identified, studies on PEGs have priority due to the extensive usage of this polymer class. Evidence suggests that non-functionalized, low molecular weight PEGs readily biodegrade in soils. However, the influence of molecular weight and end-group functionalization on biodegradation require a systematic future assessment. Conversely, high molecular weight PEGs, especially those with end-group functionalization, may exhibit limited, if any, biodegradability in agricultural soils. These PEGs may be sufficiently stable to accumulate in topsoils, migrate into deeper soil horizons or reach adjacent aquatic environments. Clearly, more studies on the transfer and transformations of unfunctionalized and functionalized PEGs in soils are warranted. While many en-

zymes in soils can target the glycosidic bond in PSacs, extensive functionalization of the sugar hydroxyl-groups may impair their breakdown, thereby lowering their biodegradability. For this class of substances, future studies should evaluate the impact of both the type and degree of functionalization on PSac stability in soils. Due to their carbon–carbon linkages, copolymers with vinylic backbones typically exhibit high stability, potentially leading to their accumulation in agricultural soils. However, some mineralization in soils has been reported for partially hydrolyzed PVAcs/PVOHs.

A significant challenge in assessing the fate of WSPs and WDPs and in monitoring their concentrations in environmental soil samples is the development and validation of analytical techniques for quantitation. Besides the analytical challenge of quantifying WSPs and WDPs if they are present at very low concentrations in soils, WSPs and WDPs that strongly adsorb to soil particle surfaces in soils may require the development of efficient water-based extraction buffers. To ensure high extraction efficiencies, these buffers may need to contain competing co-adsorbates to detach adsorbed WSPs and WDPs from the soil particle surfaces. By providing an inventory of WSP and WDP structures used in agricultural formulations, this work provides a basis for developing analytical approaches for targeted searches of the specified polymers in soil samples using suitable extraction techniques followed by detection and quantitation (*e.g.* by mass spectrometry).

Information on transfer and transformation processes will allow to define exposure scenarios and thereby help in the assessment of potential risks of WSPs and WDPs in soils. For persistent and mobile WSPs and WDPs, research on their effects may need to be extended to secondary receiving environments adjacent to agricultural fields, including aquatic systems such as streams and lakes. Charged polymers may exhibit charge-specific effects in aquatic systems.[15] For instance, negatively charged WSPs may bind cationic nutrients (*e.g.* Ca^{2+}), while positively charged WSPs and WDPs may strongly adsorb to negatively charged surfaces of aquatic organisms, such as gills.[69,70]

Persistence alone is increasingly recognized as a major concern in global chemical regulation: persistent chemicals, once released into the environment, may accumulate, leading to increasing environmental concentrations and exposure over time.[71] For this reason, the use of persistent WSPs and WDPs in agricultural formulations needs careful evaluation, particularly when these

polymers have large market volumes. Replacing these persistent polymers with soil-biodegradable alternatives is a viable strategy to overcome WSPs and WDPs accumulation in soils while, at the same time, allowing to leverage the benefits of WSPs and WDPs in agricultural formulations. Studies systematically assessing the soil biodegradability of the major WSPs and WDPs used in agricultural formulations therefore are highly warranted.

Supplementary Information

Tables 1–5 are available at https://www.chimia.ch/chimia/article/view/2023_764.

Received: September 14, 2023

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