BTO Verkennend Onderzoek

S E P T **E** D

Making invisible plastics visible: water-soluble polymers in aquatic environments

Summary

Plastic waste has progressively entered our lives, but invisible, soluble polymers, have often been disregarded as focus is set on the environmental impact of their insoluble counterparts. Soluble polymers can follow several transport routes and can consequently be found in aquatic environments. By using three examples of polymers (polyacrylamides, polyvinyl alcohol and polycarboxylates), degradation, ecotoxicology, toxicology and analytical methods are presented and discussed. The goal of this literature review is to determine to which extent these polymers pose a threat to the environment and potentially, drinking water quality. Findings from this research show that developing adequate analytical methods to analyze soluble polymers in freshwater samples are still challenging. This highlights the importance of increasing awareness about the role that persistent water-soluble polymers might play in the environment.

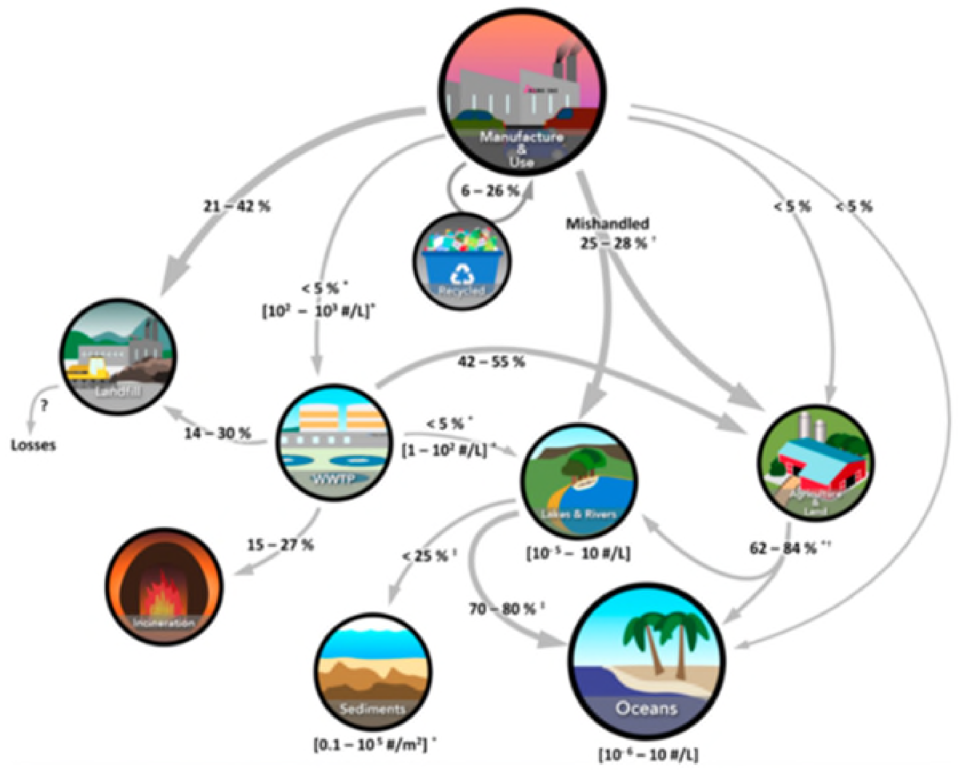

Figure 1: Estimates of plastic loading and transport pathways in the environment.[32]

Background

Since the beginning of the 20th century, non-natural polymers and synthetic materials have progressively entered our lives, with a steady growth in variety, volumes, applications and amount of non-biodegradable waste[1]. Poor management and disposal of plastic litter is a well-known problem of our society. In the beginning, attention has been on visible waste, as this is a problem many can relate to. From there it shifted to less easily spotted waste, in particular to so-called microplastics[1], defined by the European Chemical Agency, microplastics are defined as “synthetic water insoluble polymers of 5 mm or less in any dimension”[2]. Water-soluble polymers are hence not included in the latter definition[3]. However, they for instance commonly used as flocculants in wastewater treatment plants (for example fluoride (Wang et al., 2011) or arsenic remediation (Saha et al., 2012)) and, after usage, are usually disposed in landfills, incinerated or directly dumped into rivers and aquatic environments. In 2009, total communal sludge production in The Netherlands amounted to 336,000 tons of dry matter, which corresponds to approximately 3,770 tons of active polyelectrolytes (i.e., 0,5-1% active polymer or 11 g active polymer/kg dry matter)[4], part of which remains dissolved and filters into the environment. Once they reach the ecosystems, soluble polymers can follow several interrelated routes of fragmentation caused by biodegradation, oxidation, hydrolysis, photodegradation or mechanical processes. Some of these fragments can biodegrade completely and are removed from the environment due to mineralization. Other fragments may on the other hand endure unchanged. Consequently, biodegradability is gaining in importance during the design phase of new polymer (both soluble and non). Additionally, alternative natural materials, such as cationic starch, are being considered and tested[4]. In the case of water-soluble polymers already in use, it is essential to thoroughly evaluate the fate and effects that their degradation products have on the environment and human health. However, little information on the (bio)degradation of water-soluble polymers is available to date.[5,6,7]

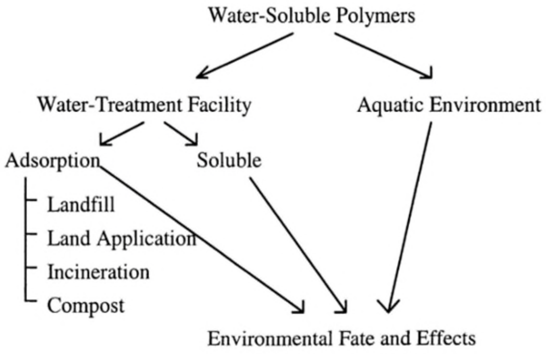

Figure 2: Environmental fate of soluble polymers

There are three main water-soluble polymers, often also called polyelectrolytes, namely: polyacrylamides (PAMs), polyvinyl alcohol (PVA) and polycarboxylates[2]. PAMs are used in different sectors, but one of their main application is as a flocculant in wastewater treatment plants (Fig. 3). PVA on the other hand, can be used as thickener in paint and in the plastic layer of sanitary towels. Polycarboxylates are used in cleaning products in order to avoid the precipitation of calcium carbonates, and can be divided in two categories: homopolymers of acrylic acid (P-AA) and copolymers of acrylic/maleic acid (P-AA/MA). Polycarboxylates are mostly found in domestic wastewater, but also in receiving waters of sewage treatment plants.

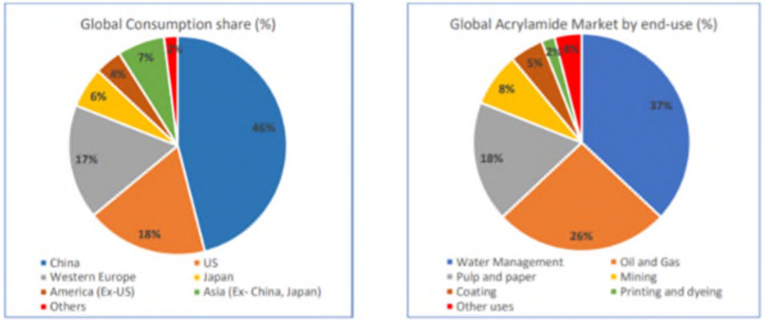

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Figure 3: Global consumption and markets of the monomer acrylamide

Degradation

There are several ways to degrade PAMs. Mechanical degradation commonly used in oil and gas industry applications, chemical degradation promoted by free radicals, thermal degradation, photolytic degradation, and biodegradation, where microorganisms utilize the amide group of the polymer as a nitrogen source and/or the carbon backbone as carbon source present in the

PAMs chain[8,9]. Chemical degradation and photodegradation of polycarboxylates are likely to happen under environmental conditions, but in general they are hydrolytically and photolytically very stable[10]. PVA on the other hand has been shown to undergo photo-oxidative degradation in UV/H2O2 photochemical reactors[11].

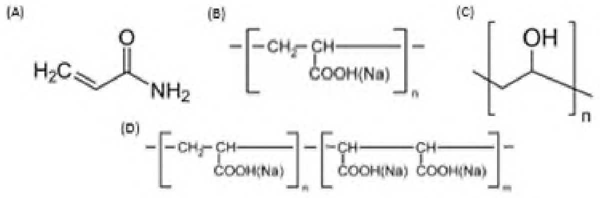
Toxicology

Polyacrylamide itself does not show a significant toxicity. The monomer acrylamide on the other hand is a mammalian genotoxic, as reported by in vitro and in vivo assays[12]. The Food and Drug Administration (FDA) and the U.S. Environmental Protection Agency (EPA) regulate acrylamide in water intended for human consumption, limiting its concentration to 0.5 µg/L, while the European Commission (EC) has a stricter limit of 0.1 µg/L. Polycarboxylates are of low toxicity by all exposure routes examined in laundry and drinking water (direct skin, indirect skin contact, inhalation, direct and indirect oral exposure). Based on the accessible information on toxicity tests on rats, it is considered that polycarboxylates do not pose any specific danger to humans[13]. PVA is benign to living tissues and thus considered non-toxic[19].

Ecotoxicology

Even though PAM is classified as non-toxic to the natural ecosystems, it significantly increases water viscosity and causes movement inhibition, decreased filtering rates and disruption of food capture mechanisms for aquatic life when the polymer is dissolved at considerably high concentrations. Acute toxicity tests show high EC_{50} values compared to natural exposure concentration in aquatic environments. P-AA have a high k_d (18,825 L/kg), which implies a high adsorption of this compound to activated sludge. Therefore, it does not show significant risk for the environment. PVA is highly soluble in water and it leaches readily from the soil into groundwater. Therefore, it can cause serious environmental problems since it has the ability to mobilize heavy metals from sediments in water streams and lakes. In a similar manner to other water-soluble polymers, conventional biological systems (e.g. activated sludge) are not adequate to decompose PVA polymer chains. Hence, alternative treatment techniques are considered in order to remove PVA from wastewater systems[11].

Figure 4: Structure of monomer acrylamide (A), P-AA (B), PVA (C) and P-AA/MA



Analytical methods

A first option for the analysis of PAM is a reverse-phase High Performance Liquid Chromatography, with UV detection, with a Limit of Detection (LOD) of 5 µg/L. Another possibility is a solid-phase extraction with activated carbon filter, followed by Gas Chromatography and Mass Spectroscopy detection (GC-MS). However, the method requires large sample volumes (i.e. 0.5L) and is thus not very sensitive. Another technique used is ion-exclusion chromatographic separation followed by MS detection[14]. These are a few options, but a standard method for freshwater samples has not been developed yet for PAMs.

The quantitative assessment of polycarboxylates in a detergent matrix is challenging, because P-AA and P-MA/AA are normally present in low concentrations (0,5-1% active polymer[4]). On top of that, surfactants have a strong tendency to form micelles and also interact strongly with polymers. Thus, it is difficult to perform analytical separation and spectroscopic characterization[15,16]. An analytical method using off-line size exclusion chromatography–nuclear magnetic resonance (NMR) combined with ethanol extraction and size exclusion chromatography has been developed[9]. The advantages of using NMR is that prior knowledge of polymer composition is not needed and quantitative results can be obtained. However, it is a highly complex analytical technique not readily available in most laboratories.

Drinking water perspective

Soluble polymers are used for the preparation of drinking water from low quality sources and in cleaning up wastewaters of domestic or industrial origin. These polymers have been utilized in coagulation and/or flocculation processes for water purification[16]. In combination with ultrafiltration membranes, they are used to remove pollutant ions from aqueous solutions[17]. Unfortunately, information about the presence of soluble polymers in drinking water is lacking and more research about their occurrence and levels needs to be carried out. For instance, it has been shown that PVA can leach from soil into groundwater[11], thus if the groundwater in question is used as a drinking water source, it could be present in drinking water.

Relevance

Soluble plastics have recently hit the spotlight. Because of their characteristics, they are easily overlooked and difficult to detect in soil, water and organisms. There is an urgent need to determine their impact on the environment, in particular as there is currently a lack of information about their occurrence and fate. For instance, PVA has been shown to leach from soil into groundwater and can thus mobilize heavy metals from sediments[11]. Because groundwaters are widely used for drinking water production, this can be a serious problem for drinking water quality. Furthermore, biological systems such as activated sludge are not adequate to decompose PVA polymer chains, hindering their removal during wastewater treatment[11]. Furthermore, the widespread use of these chemicals in wastewater treatment processes means that they can be found in receiving waters.

Important information about the use, degradation, toxicity and analytical methods to measure water-soluble polymers were presented. As these compounds are increasingly being recognized as emerging contaminants, it is important to raise awareness about their possible role as persistent contaminants in the environment. From the information found so far, acrylamide and PVA appear to be among the primary concerns due to their toxicity and capacity to mobilize heavy metals in sediments.

With regard to PAMs, there is currently no standard method for analysis in fresh-water samples. Its developing is still challenging especially considering the low concentrations and the interference of environmental impurities involved. This results in a wide inability to trace PAMs and other synthetic polymers and to determine their spread through natural waters[18]. The quantification of P-AA, P-AA/MA and PVA in aquatic samples is also still a major challenge. Therefore, there is need to develop more robust and accurate methods for their determination in environmental matrices, and in particular water.

Keywords

Plastics, polymers, watersoluble, polyacrylamides, polyvinyl alcohol, polycarboxylates, analytical chemistry

Authors

Maria Luiza Azevedo (VU), Marco Tibaldi (VU), Ruud Steenbeek (KWR), Patrick Bauerlein (KWR), Leo van Stee (KWR) and Frederic Béen (KWR)

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