

Could We Spare a Moment of the Spotlight for Persistent, Water-Soluble Polymers?

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SCIENTIFIC
OPINION
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There is currently a research spotlight on microplastic and nanoplastic to elucidate their environmental impacts. Within this spotlight is an ongoing discussion regarding which plastic materials and polymers to focus on.¹ One aspect that does appear to be gaining momentum is that only water *insoluble* polymers need be considered. This has been proposed in the pages of this journal.¹ It has also been stated in the European Chemical Agency's proposal to restrict intentionally added microplastics, defined as "synthetic water *insoluble* polymers of 5 mm or less in any dimension".² This has the implication that persistent, *water-soluble* polymers like polyacrylamides (PAM) and polycarboxylates would *ipso facto* not be considered microplastic or even nanoplastic to many researchers. Persistent, water-soluble polymers like PAM and polycarboxylates have annual production volumes well into the millions of tonnes, with many uses associated with direct environmental emissions. A potential consequence of this insoluble spotlight is that deeper insights into the fate and impacts of these persistent, water-soluble polymers will not gain as much attention as they should. This should not be the case, as many of the concerns of persistent, insoluble polymers overlap directly and indirectly with their soluble counterparts (Figure 1).

PERSISTENCY

The environmental persistency of certain water-soluble polymers like PAM and polycarboxylate are well established.^{3,4}

Direct environmental emissions of PAM come from its use as a flocculant in water treatment, as an agricultural soil conditioner, and increasingly, as a viscosity enhancer in oil and gas drilling and fracking.⁵ PAMs, polycarboxylates, and other water-soluble polymers are also used in detergents and as water-absorbing polymers in many consumer products. Degradation of these polymers occurs more rapidly under industrial or water treatment processes than under environmental conditions. This results in environmental emissions of both commercial products and lower molecular-weight breakdown products of varying persistence.^{4–6} With increasing market demand for water-soluble polymers, environmental concentrations of them and their degradation products will inevitably increase. At sufficient environmental concentrations, and lack of responsible use, these would act like flocculants and detergents in recipient waters that they were not intended for, and as conditioners of soils and sediments other than in intended areas. In extreme cases this could cause long-lasting changes to natural ecological processes, independent of direct toxicity effects, potentially reminiscent of "poorly reversible

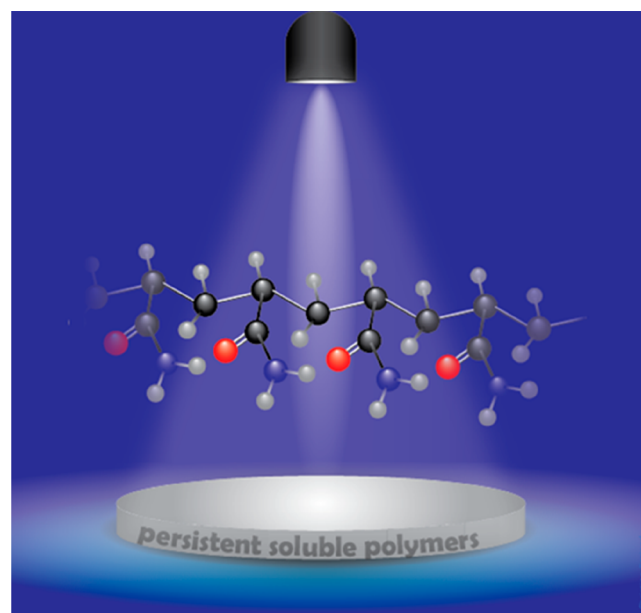


Figure 1. Persistent, water-soluble polymers in the research spotlight.

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future impacts” that have been observed for other persistent substances.⁷

■ MOBILITY AND TOXICITY

Water-soluble polymers are in general considered immobile in soil and porous media due to intensive ionic and van der Waals interactions with organic matter and minerals. However, as just presented, some will degrade to smaller, more mobile polymers, in addition to oligomers, monomers, and other chemical byproducts. An example is PAM releasing its monomer acrylamide, a potent neurotoxin, under anaerobic conditions.⁵ Because of the unknowns related to PAM degradation products, including their potential to cross or foul cell membranes, it has been recently argued that “the toxicity, transport, fate, and removal efficiency of degraded PAM needs to be re-examined in light of existing information on both PAM and the acrylamide monomer.”⁵ In the oil-and-gas industry, concentrations of degraded PAM in wastewater have been reported at 10–1000 mg/L,⁵ which is at levels where acute ecotoxic effects have been reported.⁸

■ TRANSCENDING CUT-OFFS

There is no real size cutoff border between an insoluble nanoplastic and a soluble nanoplastic, for example degraded PAM ranges from 18 to 350 nm in size.⁶ Further, soluble and insoluble complexes can agglomerate to make polymeric nanocomposites.⁹ Therefore, methods like size exclusion chromatography and field flow fractionation capture both.

These polymers may appear at the microscale as well. PAM itself is increasingly being reported as a solid microplastic found in environmental samples including marine turtles and beach sand.^{10,11} The origins of these PAM particles are unclear, they could be insoluble PAM from low pH synthesis,¹² large cross-linked structures of PAM,^{9,12} flocculated composites of mostly PAM or PAM coated particles; there is potential complexity here in terms of the soluble becoming insoluble in the environment through flocculation or other processes.

■ MITIGATING MICROPLASTIC EMISSIONS WITH WATER-SOLUBLE POLYMERS

There are intriguing aspects to further consider regarding the use of soluble polymers for the management of suspended particulate matter (SPM) and colloids. Both SPM and naturally occurring colloids are toxic to aquatic life at sufficient concentrations, and it is a central question for the research spotlight on microplastic and nanoplastic if they are more toxic than natural SPM and colloids within specific environments or not.

When water-soluble polymers are used to lower the SPM and colloidal concentrations in wastewater, such as for turbidity control, they would also lower the insoluble microplastic concentration in wastewater through this process. At the same time, the produced sludge or flocculated sediment would be enriched with both soluble and insoluble polymers. If this sludge was further used as a fertilizer, additional water-soluble polymers may be applied as soil conditioners to prevent erosion. This, too, would prevent the spread of insoluble microplastics via the agriculture runoff, but have the net effect of increasing the concentration of persistent, synthetic polymers in the soil with each application of sludge and soil-conditioner.

In this way, water-soluble polymers appear to have great potential to mitigate emissions of insoluble microplastics and nanoplastic, as well as other contaminants,⁹ into receiving waters. However, further research is needed to ensure such technology avoids potential risks from emissions into unintended environments, as mentioned above, as well as to investigate the potential combined impacts of co-occurring insoluble and soluble polymers in soil and sediment.

■ SHARE THE SPOTLIGHT

Persistent, water-soluble polymers being outside the predominant definition of microplastic does not mean they should be ignored. Many analytical techniques are suitable for both insoluble and water-soluble polymers, including size exclusion chromatography, infrared spectroscopy, and mass spectroscopy. In many environmental samples, both types of synthetic polymers can co-occur. Understanding the environmental behavior of water-soluble polymers will help us better understand the behavior of insoluble polymers, and how to avoid harmful environmental impacts thereof. The spotlight should shine on all persistent polymers.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Hartmann, N. B.; Hüffer, T.; Thompson, R. C.; Hasselöv, M.; Verschoor, A.; Dugaard, A. E.; Rist, S.; Karlsson, T.; Brennholt, N.; Cole, M. Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. *Environ. Sci. Technol.* **2019**, *53* (3), 1039–1047.
- (2) ECHA Annex XV Restriction Report - Proposal for a Restriction: Intentionally added microplastics. Version 1.2. (<https://echa.europa.eu/documents/10162/05bd96e3-b969-0a7c-c6d0-441182893720>) (accessed November 7, 2019); 2019.
- (3) Hennecke, D.; Bauer, A.; Herrchen, M.; Wischerhoff, E.; Gores, F. Cationic polyacrylamide copolymers (PAMs): environmental half life determination in sludge-treated soil. *Environ. Sci. Eur.* **2018**, *30* (1), 16.
- (4) Jop, K. M.; Guiney, P. D.; Christensen, K. P.; Silberhorn, E. M. Environmental Fate Assessment of Two Synthetic Polycarboxylate Polymers. *Ecotoxicol. Environ. Saf.* **1997**, *37* (3), 229–237.
- (5) Xiong, B.; Loss, R. D.; Shields, D.; Pawlik, T.; Hochreiter, R.; Zydny, A. L.; Kumar, M. Polyacrylamide degradation and its implications in environmental systems. *NPJ. Clean Water* **2018**, *1* (1), 1–9.
- (6) Xiong, B.; Miller, Z.; Roman-White, S.; Tasker, T.; Farina, B.; Piechowicz, B.; Burgos, W. D.; Joshi, P.; Zhu, L.; Gorski, C. A. Chemical degradation of polyacrylamide during hydraulic fracturing. *Environ. Sci. Technol.* **2018**, *52* (1), 327–336.
- (7) Cousins, I. T.; Ng, C. A.; Wang, Z.; Scheringer, M. Why is high persistence alone a major cause of concern? *Environmental Science: Processes & Impacts* **2019**, *21* (5), 781–792.
- (8) Buczek, S. B.; Cope, W. G.; McLaughlin, R. A.; Kwak, T. J. Acute toxicity of polyacrylamide flocculants to early life stages of freshwater mussels. *Environ. Toxicol. Chem.* **2017**, *36* (10), 2715–2721.
- (9) Rivas, B. L.; Urbano, B. F.; Sánchez, J. Water-soluble and insoluble polymers, nanoparticles, nanocomposites and hybrids with ability to remove hazardous inorganic pollutants in water. *Front. Chem.* **2018**, *6*. DOI: 10.3389/fchem.2018.00320

(10) Duncan, E. M.; Broderick, A. C.; Fuller, W. J.; Galloway, T. S.; Godfrey, M. H.; Hamann, M.; Limpus, C. J.; Lindeque, P. K.; Mayes, A. G.; Omeyer, L. C. Microplastic ingestion ubiquitous in marine turtles. *Global change biology* **2019**, *25* (2), 744–752.

(11) de Jesus Piñon-Colin, T.; Rodriguez-Jimenez, R.; Pastrana-Corral, M. A.; Rogel-Hernandez, E.; Wakida, F. T. Microplastics on sandy beaches of the Baja California Peninsula, Mexico. *Mar. Pollut. Bull.* **2018**, *131*, 63–71.

(12) Berndt, W.; Bergfeld, W.; Boutwell, R.; Carlton, W.; Hoffmann, D.; Schroeter, A.; Shank, R. Final report on the safety assessment of polyacrylamide. *J. Am. Coll. Toxicol.* **1991**, *10* (1), 193–203.