OVERVIEW OF AQUATIC RISK ASSESSMENT OF POLYMERS – EVIDENCE FROM CATIONIC POLYMERS

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WHAT ARE POLYMERS?

- **Large macromolecule**, mostly >1000s Da., with at least 3 covalently bound monomers
- Many different uses depending upon their designed properties:
  - Pharmaceutical; nano; cleaning; biocides; lubricants; plastics; flocculants etc.
- **Different types** of polymers:
  - Natural (DNA; starch; sugar etc.) and industrial biopolymers
  - Synthetic e.g. in chemical industries, plastics and rubbers
  - Different functionalities and properties
- **Different compositions**:
  - A mixture of monomers, smaller polymers and large polymers, impurities
  - Additives – e.g. stabilizers
- **So, what are they?**:
  - UVCB’s; drugs; nanomaterials; microplastics?
  - Answer: Depends on the specific polymer
WHY POLYMERS?

- Large global volume and increasing uses – today they are a multi-million dollar industry
- First real regulatory interest in the 1990s by OECD - USEPA assessment and prioritization in TSCA in 1996 Boethling and Nabholz (1996) summarized hundreds of regulatory submissions from 1980s to 1995 and developed USEPA position
- Polymer exemption from registration in certain regulatory programs (e.g., REACH) due to assumed low concern - these assumptions are now being reconsidered
- Toxicity and exposure is unknown for the most part – high persistence is however known
POLYMERS OF TOXICOLOGICAL CONCERN

Characteristics:

• Backbone and composition (natural, carbon, silicon)
  • No clear differences in toxicity
• Molecular weight (MW) and distribution (Lipinski’s rule on bioavailability)
  • MW > 1000 Dalton → low concern (cannot pass cell membranes)
  • MW < 1000 Dalton and >1% oligomers → potential concern
• Charge and ionic properties
  • Cationic polymers are of potential concern due to aquatic toxicity (e.g. PQ6)
• Size
  • If they can degrade to smaller molecules → potential concern
• Functions and functionalizations
  • Biocidal or other functions, additions and substitutions → potential concern
• Solubility (water and lipids)
  • If they can overcome Lipinski’s rule → potential concern
SciFinder review: “Cationic + polymer + aquatic + toxicity” = 7 hits → not much data!
CATIONIC POLYMERS CURATED REVIEW

Curated review returned 50 relevant aquatic tox. publications (1970-2019) – not much data
Distribution of published acute toxicity data for the PQ10 (mixed polymer) and mainly acute toxicity PQ6 (homopolymer (PolyDADMAC)) (Pecquet et al. 2019):

→ Quite large variations in toxicities (nom. concentrations)
Boethling and Nabholz (1996) reported 21 blinded cationic polymer datasets with associated important toxicity descriptor information:

- For acute fish there is a clear positive relationship between charge density and toxicity and negative relationship between MW and toxicity - not so clear for Daphnia and algae - algae toxicity ranges from 0.006 to 1000 mg/L!
- Log Kow is not a good descriptor
- Acute to Chronic Ratios = 14-18 → not specific MoA
TOXICOLOGICAL CHALLENGES

- Lack of publicly available data!
- Uncertainty about MoA – physical effects and modelling dose-response?
- Uncertainty about toxicological bioavailability?
- What are the relevant toxicological descriptors?
- Are these UVCBs – and how to test mixtures?
- Test methods – do they need update/amendments?
- Mitigating factors – humic acid, solids, in the tests – guidance?
- Need analytical methods to verify exposures!
- Need to develop computational models when the above is resolved?

→ Need consensus and guidelines for these issues
QSAR MODELLING?

- Follow OECD principles?
- Lack of ecotox data → 2d fragment based QSAR modelling – ongoing work
- Other models can other descriptors be transferred – ongoing work
Canada: Polymers in CEPA (2001) – determine if the polymer is of low concern – mainly volume; WS (Log Kow); algal toxicity. See poster by ECCC (MP074) for updates.

USA: Three categories for soluble polymers:
1. Low MW → can assess toxicity
2. Large polymers with low MW → can maybe assess toxicity
3. Large polymer with high MW → consider physical effects

Europe: ECHA is reviewing how to prioritize the polymers of concern – need data which is not currently publicly available. Knowing that toxicity assessments are less suited and that sound ecotox models does not exist – issues needs solving?

Environmental relevance and mitigating factors of the tests needs clarification and optimization (?) – guidance...
CONCLUSIONS

Ongoing work see the next presentations and follow the iTAP project:

SETAC-Europe session: Environmental Risk assessment of Polymers

Under track 4: Ecological risk assessment and human health risk assessment of chemicals, mixtures and stressors and risk mitigation strategies

Abstract deadline: Nov 27th!
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