CEFIC Long-range Research Initiative
Request for Proposals (RfP)

Title and Code Number:

Improving the environmental (aquatic) hazard and risk assessment of cationic polymers – **LRI ECO46**

Background

Cationic substances released in the environment can sorb to negatively charged particulate or dissolved matter, *e.g.* humic acids, microorganisms, algae, clay and silica. Those sorption properties can significantly affect the bioavailability and thus apparent toxicity of cationic substances to aquatic organisms. Part of the adverse effects observed can be attributed to indirect (physical) effects resulting, for example, from the clogging of respiratory organs such as gills. This is especially true for cationic polymers which are not expected to pass biological membranes and are rather expected to affect the outer membranes of aquatic organisms, or their near environment (Nabholz & Zeeman, 1991; Cumming, 2007, 2008).

Dissolved Organic Carbon (DOC) species such as humic acids can reduce the apparent toxicity of cationic polymers by one or two orders of magnitude (Cary *et al.*, 1987, 1989). This mitigation effect has been known for decades and is considered since the 90's in US testing guidelines (*e.g.* OPPTS 850.1085 Fish Acute Toxicity Mitigated by Humic Acid – EPA, 1996) and regulatory assessment procedures (*e.g.* Environmental Assessment of Polymers under the U.S. Toxic Substances Control Act – Boethling & Nabholz, 1997). The situation is quite different in Europe as there is no guidance at the moment on the way cationic substances should be tested and assessed. Shall ecotoxicity tests be performed with tap water, tap water supplemented with humic acids, or river water? Shall toxicity measurements be based on dissolved or freely dissolved concentrations? The situation is all the more complex as there is a lack of consistency between OECD testing guidelines regarding the characteristics of acceptable dilution waters (e.g. the concentration in Total Organic Carbon).

If truly bioavailable concentrations of cationic polymers are not determined in an appropriate way, this can lead not only to an erroneous estimation of aquatic hazards but also to an erroneous estimation of exposures and risks. For example, if experimental toxicity data obtained with tap water are directly compared with exposure concentrations measured in the field, this might lead to an overestimation of risks if no distinction is made between freely dissolved and DOC-sorbed polymer concentrations. To better assess bioavailable concentrations, Solid-Phase MicroExtraction (SPME) method could be used to monitor the freely dissolved concentrations of polymers (Andersson, 2012). This method has already been demonstrated to allow reliable measurements of the freely dissolved concentrations of cationic surfactants in various environmental samples (Chen *et al.*, 2012, 2013). Alternatively, ECETOC (2003) proposes to follow a *bulk approach* relying on modified ecotoxicity tests with humic acids on one side, and on field measurements addressing total concentrations (bulk = dissolved and sorbed) on the other side. However, ECETOC provides only general orientations and gives no methodological scheme. In addition, while performing risk assessments, exposure concentrations are

most often derived from *in silico* predicted data provided by models (*e.g.* EUSES) rather than from *in situ* measurements. But are those models applicable to cationic polymers? Besides, if the sorbing behavior of cationic polymers cannot be appropriately predicted, how can we expect the exposure and risk assessments to be accurate?

Objectives

The project aims at assessing in a realistic and consistent way the environmental threat posed by cationic polymers. A first objective is to provide a review of the various methods and tools currently available to measure or predict the toxic and fate properties of cationic polymers (*e.g.* standard guidelines, sampling methods, SAR equations, fate models, etc.). A second objective is to clarify the methodological scheme that should (or shall) be followed when assessing cationic polymers:

1. Environmental hazards: definition of the characteristics of appropriate dilution waters (*i.e.* tap water, tap water supplemented with humic acids, or river water) for standards and modified ecotoxicity tests; recommendation of methods for the appropriate monitoring of bioavailable concentrations; proposition of mitigation factors to be used when deriving classification from tests run with river water;

2. Environmental risks: thorough description of the bulk approach; review of exposure models' applicability to cationic polymers; proposition of mitigation factors to be used when deriving $PNEC_{aqua}$ from tests run with tap water.

Scope

The project aims at providing a common methodological approach to assess the environmental hazards and risks associated with the water release of cationic polymers, *e.g.* polyquaterniums (PQ-6, PQ-10, etc.), dimethylamine-epichlorohydrin copolymer or guar hydroxypropylrimonium chloride. The recommended methodological approach will be established from a state-of-art review of the toxic and fate properties of cationic polymers, and of the ways to assess these properties in a regulatory context. The definition of "hazard" and "toxicity" *(i.e.* "means the intrinsic property of a substance to cause adverse effects to aquatic species" – CLP Regulation), as well as the concept of bioavailability, will be at the core of the discussions when questioning the relevancy of toxicity tests performed with humic acids. The project could include an experimental phase dedicated to SPME sampling methods in order to compare toxic effects expressed either based on total or freely dissolved concentrations of polymers. The project could build on the work of Y. Chen, S. T. Droge and J. L. Hermens towards a better understanding of the partition behavior of cationic surfactants (Chen *et al.*, 2012, 2013) as part of the ERASM project on the bioavailability of cationic surfactants[1].

[1] http://www.erasm.org/bioavailability/erasm-research/project/partitioning-behavior-of-cationic-surfactants

Cost and Timing

Start in 2018
Duration: 3 years
Budget in the order of €250K.

Partnering/Co-funding

Applicants should provide an indication of additional partners and funding opportunities that can be appropriately leveraged as part of their proposal. Partners can include, but are not limited to industry, government/regulatory organizations, research institutes, etc.. Statements from potential partners should be included in the proposal package.

Fit with LRI objectives/Possible regulatory and policy impact involvements/ Dissemination

The project aims at providing recommendations which could be used as a basis to augment key standards and regulatory guidance used in EU to test and assess the environmental hazards of chemicals, for example:

- update of the OECD TG 203 with inclusion of limited DOC contents for tests run with river water;
- update of the « Guidance on application of CLP criteria » to include specific recommendations for cationic polymeric substances, especially regarding the acceptability of toxicity tests run with humic acids.

Besides, the recommendations could be used as a basis for future orientations on the hazard and risk assessment of polymers. As a result, the project could be addressed as part of the LRI topic dedicated to the “Improved environmental framework for characterization and assessment of polymers” (Other 3). Eventually, the recommendations first developed for cationic polymers could be later extended to all cationic substances.

References

Andersson M. (2012). Acute toxicity to Daphnia magna in river water. Investigating mitigation and bioavailability of pure cationic surfactants and mixtures with SPME. Master thesis, University of Gothenburg.

Boethling R.S. & Nabholz J.V (1997). ‘Environmental Assessment of Polymers under the U.S. Toxic Substances Control Act’, in: Ecological Assessment of Polymers Strategies for Product Stewardship and Regulatory Programs, pp. 187-234. Hamilton, J. D. & Sutcliffe R. (eds.), Van Nostrand Reinhold.

Cary G. A., McMahon J. A. & Kuc W. J. (1987). The effect of suspended solids and naturally occurring dissolved organis in reducing the acute toxicities of cationic polyelectrolytes to aquatic organisms. Environmental Toxicology and Chemistry, 6 (6), 469-474.

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Cary G. A., Kuc W .J. & McMahon J. A. (1989). Toxicity of cationic polyelectrolytes to aquatic organisms – The relationship between acute toxicity and dissolved organic carbon. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry), 30 (2), 384-385.

Chen Y., Droge S. T. & Hermens J. L. (2012). Analyzing freely dissolved concentrations of cationic surfactant utilizing ion-exchange capability of polyacrylate coated solid-phase microextraction fibers. Journal of Chromatography A, 1252, 15-22.

Chen Y., Hermens J. L. & Droge S. T. (2013). Towards a better understanding of the bioavailability and partition behaviour of cationic surfactants. Draft Final Report of the Contribution from IRAS, Utrecht University. APAG KUG Research Project 804 (available on www.erasm.org).

Cumming J. (2007). 'Polyelectrolytes', in: Chemical of Concern in Wastewater Treatment Plant Effluent. CRC for Water Quality and Treatment, Occasional Paper No. 8, pp. 57-68. Cooperative Research Centre for Water Quality and Treatment, Adelaide.

Cumming J. (2008). Environmental Fate, Aquatic Toxicology and Risk Assessment of Polymeric Quaternary Ammonium Salts from Cosmetic Uses. Doctoral thesis, Griffith School of Environment, Griffith University.

ECETOC (2003). 'Sorptive substances', in: Environmental Risk Assessment of Difficult Substances, Technical Report No. 88, Chapter 4, pp. 33-52. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels.

EPA (1996). OPPTS 850.1085 Fish Acute Toxicity Mitigated by Humic Acid. Ecological Effects Test Guidelines. Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency, Washington D.C.

DEADLINE FOR SUBMISSIONS: 31 August 2017

Please see www.cefic-lri.org for general LRI objectives information, project proposal form and further guidance for grant applications.