Degradation of antifouling booster biocides evaluated with bioassay

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Summary

Some organic booster biocides are intended as replacement for the highly toxic antifouling agent tributyltin, which has been regulated internationally. Zinc pyrithione (ZnPT) has been used as antifouling agents for ship hull as well as as antidandruff stuff in shampoo. Copper pyrithione (CuPT) is likely used only for antifoulants. There is little information available on the environmental fate and ecotoxicity of the metal pyrithiones. Another difficulty is a lack of chemical analysis established for them. In this study, photodegradation of the pyrithiones was evaluated with bioassay in terms of toxicity alteration. Two bioassays, sea urchin egg development test and freshwater rotifer lethality test, were employed for the pyrithiones, which were irradiated with UV-A lamp for up to two hours.

The 27-h EC_{50}s of ZnPT and CuPT on sea urchin were 7~10 fg/L and 2.3 ng/L, respectively. The toxicity of ZnPT was extremely high but dramatically decreased (2.1 ng/L as EC_{50}) only by solvent evaporation without irradiation. This phenomena was not observed for CuPT. Weaker toxicity was observed with longer irradiation period for both compounds. The toxicities of 2-hour irradiated ZnPT and CuPT decreased in comparison with the controls but were much higher than the toxicity of each metal, although their UV spectra suggested significant destruction of their mother moiety. Some intermediates produced by photochemical reaction may have contributed the toxicity. The 24-hour LC_{50}s of ZnPT and CuPT on rotifer were 12 μg/L and 5 μg/L, respectively. CuPT gave a slightly higher toxicity to rotifer than ZnPT did. It was, however, apparent that the sensitivity of freshwater rotifer test to metal pyrithiones was much lower than that of sea urchin test. There was no change in toxicity by solvent evaporation without irradiation and weaker toxicity was observed with longer irradiation period for both compounds. The toxicity of 2-hour irradiated ZnPT dramatically decreased to give no mortality at the highest concentration tested (100 μg/L). On the other hand, the LC_{50} of 2-hour irradiated CuPT was 29 μg/L although the UV spectra suggested significant destruction of their mother moiety. This suggests that some photochemical intermediates contributed the toxicity. Thus, the bioassay could evaluate the degradation of metal pyrithiones by photochemical reaction. It is needed to clarify what the intermediates are by using both chemical analysis and bioassay.