UNIVERSITY GRADUATE SCHOOL BULLETIN ANNOUNCEMENT

Florida International University
University Graduate School

Doctoral Dissertation Defense

Abstract

Assessment of the Toxicity of Legacy and Next-Generation Perfluoroalkyl Substances (PFAS) in Early-Life Stages of Freshwater and Marine Fish

by

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Per- and polyfluoroalkyl substances (PFASs) are a group of synthetic surfactants that have utilized for several decades in a wide range of industrial and manufacturing applications. Owing to their high chemical stability, PFAS are widespread and persistent in the environment, and have been shown to be bioaccumulative in diverse organisms including plants, wildlife, and humans. At the same time, exposure to PFASs has been linked to a range of documented toxic and/or adverse effects in relation to human and animal health. While so-called "legacy" PFAS including, in particular, long-chain perfluorinated carboxylic acids and sulfonic acids which have been most widely used in the past have been phased-out, they have been replaced by a growing number of "next generation" chemical variants including short-chain, and otherwise chemically modified, representatives. The potential environmental health and ecotoxicity of next-generation PFAS remain, however, largely unclear. In the present study, toxicity, and bioconcentration potential, of several perfluoroether carboxylic acids (PFECA), as emerging pollutants of concern, in early life stages of marine and freshwater fish including a laboratory model – namely the zebrafish (*Danio rerio*) – as well as ecologically and commercially relevant species, and specifically Mahi-Mahi (*Coryphaena hippurus*) and Olive Flounder (*Paralichthys olivaceus*) was assessed. Toxicity including lethality, behavioral and developmental effects of PFECA, and the legacy PFAS, perfluorooctanoic acid (PFOA), was assessed in embryonic stages of zebrafish, alongside high-resolution magic angle spin nuclear magnetic resonance (HRMAS NMR) metabolomics techniques to elucidate metabolic pathways affected by PFAS. These studies identified acute embryotoxicity (i.e., lethality), as well behavioral and developmental effects, in the nominal micromolar range for all PFAS tested, which was correlated with fluoroalkyl chain length (and relative lipophilicity, i.e., log P), and suggested quantitatively comparable toxicity for next-generation (i.e, PFECA) and legacy (i.e., PFOA) variants. Metabolomic studies indicated targeting of liver, and specifically mitochondria, and associated metabolic (e.g., carbohydrate, amino acid and lipid) pathways. Subsequently, toxicity assays were developed and applied to early life stages of mahi-mahi to assess toxicity of PFECA and PFOA. Mahi-mahi embryos were significantly more sensitive to PFAS with lethal concentrations extending into the environmentally relevant (e.g., parts-per-billion) concentration range. Finally, toxicity and bioconcentration of PFECA and PFOA were comparatively assessed in embryos of zebrafish and flounder, as an ecologically and commercially relevant benthic marine species. These studies measured bioconcentration factors (BCF) ranging from 83 to 226-fold and 22 to 329-fold bioconcentration (relative to measured concentration in water) in embryos of zebrafish and flounder, respectively, with BCF values significantly correlated with fluoroalkyl chain length and log P values, in both cases. Toxicity similarly correlated with chain length (and log P) and supports a role of the fluoroalkyl chain length (and relative hydrophobicity) in the relative uptake, and consequent toxicity of PFAS. Notably, the BCF and toxicity of PFOA was equal to, or lower than, several PFECA, and further suggests that legacy and next-generation PFAS have quantitatively and qualitatively similar toxic potential as environmental pollutants. These findings raise concerns regarding PFECA as environmental toxicants, and specifically, as next generation replacements to legacy PFAS.

Date: June 29, 2022.
Time: 10:00 a.m.
Place: MMC – CP 320

Department: Chemistry and Biochemistry
Major Professor: Dr. John P. Berry
Zoom Meeting ID: 939 8869 4785
Passcode: PFAS22