

## Differential Toxicity and Accumulation of Fipronil Enantiomers in the Fathead Minnow (*Pimephales promelas*)

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Fipronil is a chiral insecticide applied as a racemate of two enantiomers. Because of its high log  $K_{OC}$ , fipronil will be found primarily in sediments of aquatic environments. Although a number of studies have examined toxicity in aquatic invertebrates, data on enantioselective toxicity and bioaccumulation in fish are limited. We characterized the toxicity of fipronil racemate and enantiomers in acute and subchronic aquatic toxicity experiments and measured bioaccumulation of fipronil from spiked sediments in chronic exposures with larval fathead minnows (*Pimephales promelas*). Enantioselective toxicity was observed in fathead minnows after 7 days, with higher toxicity of the racemate and (+) enantiomer (LC50s = 191 and 207 ppb) compared to the (-) enantiomer (312 ppb). Greater reductions in fish growth were also observed in fish exposed to the (+) enantiomer and racemate. In the chronic exposure, fipronil concentrations in sediment declined from 2.02 ppm at day one to 0.06 ppm after five weeks and none detected by week six. Fipronil was readily accumulated by fish, with peak concentrations (2.71 ppm) measured at one week, decreasing to 0.05 ppm by week six. The major metabolite detected in fish was fipronil sulfone. The enantiomeric fraction of fipronil was >0.50 in all samples, indicating enantioselection of the (+) enantiomer in fish tissues. Enrichment of the (+) enantiomer likely resulted from increased uptake of this enantiomer from water and sediments or increased biotransformation and/or excretion of the (-) enantiomer. These results concur with the trend observed in the acute experiments in which the greatest toxicity (mortality and growth inhibition) was observed upon exposures to the (+) enantiomer and racemate. Results support field application of fipronil enriched in the (-) enantiomer, which may serve to protect nontarget organisms such as fish from toxicity.