Pyrethroids are chiral insecticides characterized by stereoisomerism, which occurs due to the presence of one to three asymmetric (chiral) carbons, generating one or two pairs of cis/trans diastereomers, and two or four pairs of enantiomers. Diastereomers have equal chemical properties and different physical properties, while enantiomer pairs, have the same physicochemical properties, with exception by the ability to deviate the plane of polarized light to the right or to the left. However, stereoisomers exhibit different toxicities at the metabolic level, presenting enzyme and receptor selectivity in biological systems. Studies in aquatic organisms have shown that toxic effects are caused by specific enantiomers (1R–cis and 1R–trans) and that those cause potential estrogenic effects (1S–cis and 1S–trans). In this context, the same compound can have wide–ranging effects in organisms. Therefore, several studies have highlighted pyrethroid stereochemical selectivity in different environmental matrices. The analytical ability to distinguish the diastereomeric and enantiomeric patterns of these compounds is fundamental for understanding the processes of biotransformation, degradation environmental behavior and ecotoxicological impacts. In this context, a pyrethroid stereochemical approach is recommended and therefore should be included in future risk assessments and regulatory decisions.