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Enantioselective fractionation of fluoroquinolones in the aqueous environment using chiral liquid chromatography coupled with tandem mass spectrometry

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Abstract

This paper aims to examine the multiresidue enantiomeric profiling of (fluoro)quinolones and their metabolites in solid and liquid environmental matrices using chiral HPLC-MS/MS method and a CHIRALCEL® OZ-RH column. Simultaneous chiral separation was obtained for chiral ofloxacin and its main metabolites ofloxacin-*N*-oxide and desmethyl-ofloxacin; moxifloxacin; the prodrug prulifloxacin and its active compound ulifloxacin; flumequine; nadifloxacin and *R*-(+)-besifloxacin. Achiral antibiotics (ciprofloxacin, norfloxacin and nalidixic acid) were also included in the method to enable the analysis of all targeted quinolones within one analytical run. Satisfactory enantiomeric resolution (Rs $\geq$ 1) was obtained for five out of eight chiral drugs enabling quantitative analysis. The overall performance of the method was satisfactory with a method precision <20%, relative recoveries >70% for most of the analytes and method detection limits (MDL) at low ng L^{-1} levels (0.1 < MDL (ng L^{-1})< 6.4, 0.1 < MDL (ng L^{-1})< 6.6 and 0.1 < MDL (ng L^{-1})< 7.0 in influent, effluent and river waters for 83% compounds, 0.01 < MDL (ng g^{-1})< 4.9 in solids for 91% compounds). Enantiomeric profiling from a week-long monitoring campaign in the UK showed that (±)-ofloxacin was found to be racemic in upstream waters but it was enriched with *S*-(-)-enantiomer in wastewater and in receiving waters. This could be due to the fact that ofloxacin can be used both as a racemate and as a *S*-(-)-enantiomer. Its consumption was further confirmed by the chiral signature of the investigated ofloxacin metabolites. As a result, alterations in the enantiomeric composition of antibiotics could influence not only their activity and toxicity in the environment, but also could induce changes in the microbial communities constantly exposed to them.