# Contamination of benthic invertebrates and fish by perfluorinated compounds in the Rhone River (France)

## Contamination d'invertébrés benthiques et poissons du Rhône par des composés perfluorés

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## RÉSUMÉ

Depuis 2001, la classe de composés d'intérêt émergent per- et polyfluorés (PFAS) suscite beaucoup d'intérêt, eu égard à leurs usages nombreux et variés, et à leurs propriétés, notamment persistance et bioaccumulation. A la suite d'une première étude (2009-2010) sur la contamination des poissons à l'échelle du bassin du Rhône, un projet s'intéressant aux réseaux trophiques de plusieurs espèces de cyprinidés est en cours depuis 2011 dans le Rhône, à l'aval d'importantes sources industrielles de PFAS. Les données collectées dans ce cadre permettent d'expliquer, au moins en partie, le rôle de différents facteurs écologiques et environnementaux vis-à-vis de la bioaccumulation des PFAS.

## ABSTRACT

Since 2001 onwards, per- and polyfluorinated chemicals (PFASs) constitute a specific class of compounds of emerging concern, due to their numerous uses, as well as to their properties of persistence and bioaccumulation. Following a screening study at the Rhone watershed scale based on fish in 2009-2010, a research focusing on the trophic networks of several cyprinid fish species is being implemented since 2011 in the Rhone River, downstream of major PFASs industrial sources. The data gathered in this context allow explaining, though still partially, the role of different environmental and ecological factors in the bioaccumulation process of these compounds.

## MOTS CLES

emerging contaminants, perfluorinated compounds, aquatic invertebrates, fish, biomagnification

# 1 INTRODUCTION & OBJECTIVES

Since 2001 onwards, per- and polyfluorinated chemicals (PFASs) constitute a specific class of compounds of emerging concern, due to their numerous uses, as well as to their properties of persistence and bioaccumulation and their worldwide presence in environmental media (Houde *et al.*, 2011). Following a screening study at the watershed scale in 2009-2010 addressing fish contamination (Babut *et al.*, 2011), a research focusing on the trophic networks of three cyprinid fish species, namely the barbel (*Barbus barbus*), the gudgeon (*Gobio gobio*) and the roach (*Rutilus rutilus*) is being implemented since 2011 in the Rhone River, downstream of major per- and polyfluoroalkyl (PFASs) industrial sources. The study aims to describe the contamination pattern and its variations through the respective food-webs, and identify environmental and biological factors, as well as chemicals' properties, contributing to these variations.

# 2 METHODS

Surface sediments were sampled repeatedly between December 2011 and November 2013 with a van Veen grab sampler. Benthic invertebrates were collected with a truble in shallow habitats in October 2012, June and October 2013. Fish were caught by electrofishing in October 2011; a complementary set of barbels was captured with nets in November 2011.

Fish stomach contents were characterized, whenever possible. All samples were freeze-dried and finely ground. Sediment and biota samples were sonicated, centrifuged and purified using solid-phase extraction and carbon cartridges, eluted and concentrated prior to analysis. PFASs were analyzed by high performance liquid chromatography followed by tandem mass spectrometry (LC-MS/MS). $\delta^{13}C$, and $\delta^{15}N$ were determined by Isotopic Ratio Mass Spectrometry on de-carbonated sediment and in biota samples.

# 3 RESULTS & DISCUSSION

Whatever the kind of sample, the contamination profiles were dominated by long-chain perfluorinated carbon (i.e. ≥ 8) compounds. The total concentration in sediments (N=7) was rather high compared to other French rivers, but remained comparable to other European rivers or estuaries. Among the invertebrate taxa (N=12), gammarids displayed generally the highest contamination level, above oligochaetes, odonates or freshwater shrimps. Chironomids were systematically the least contaminated. When the sum of measured PFASs was considered, the barbels were significantly more contaminated than gudgeons and roaches, but the respective ranks varied depending of the compound. Several perfluorinated alkyl sulfonates were more frequently detected in gudgeons, compared to other species. Interspecies differences in accumulation were related to different feeding behaviors, as shown by the analysis of stomach contents. Nevertheless, fish physiology might also be concerned, as suggested by the comparison of accumulation patterns in the two groups of barbels (young ones captured by electrofishing, and bigger ones caught with nets).

Biota to sediment accumulation factors (BSAFs) were tentatively determined by calculating the ratios between concentrations in biota and sediment. As the organic carbon content is possibly controlling the adsorption of some PFASs by sediment (Zhao *et al.*, 2012), the refined BSAFs estimates should account for this factor.

Biomagnification factors (BMFs) were determined for two pairs of predator-prey, namely gudgeon (*G. gobio*) - chironomids, and barbel – gammarids. PFNA (perfluorononanoic acid), PFUnDA (perfluoroundecanoic acid), PFTrDA (perfluorotridecanoic acid), PFOS (perfluorooctane sulfonate) and FOSA (Perfluorooctane sulfonamide) BMFs were clearly above 1 for gudgeons, much higher than for barbels, because concentrations in chironomids were lower than in gammarids. These BMFs estimates were based on concentrations measured in fish dorsal muscles, leading to an overestimation of BMF values. This would not change the conclusion for gudgeon BMFs; conversely for PFASs having less than 11 perfluorinated carbons the biomagnification in barbels appears more uncertain. Trophic magnification factors (TMFs) which account for the whole fish diet, could help to resolve this issue.

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