A summary of available data on fish contamination by chemicals of emerging concern in the Rhone and its tributaries

Synthèse des connaissances disponibles sur les contaminants d'intérêt émergent dans les poissons du Rhône et ses affluents

Marc BABUT[1], Cécile MIEGE[2], Marina COQUERY[2], Annie PERETTI[1-2], Pierre LABADIE[3], Hélène BUDZINSKI[4], Bruno Le BIZEC[5], Katrin VORKAMP[6], and Jacek TRONCZYŃSKI[7]

[1] Irstea, UR MALY, 3bis Quai Chauveau, CP 220, 69336 LYON Cedex 9 (France) – Ecotoxicology laboratory (marc.babut@irstea.fr)
[2] Irstea, UR MALY, 3bis Quai Chauveau, CP 220, 69336 LYON Cedex 9 (France) – LAMA (cecile.miege@irstea.fr ; marina.coquery@irstea.fr)
[3] Univ Bordeaux, EPOC, UMR 5805, 351 cours de la Libération, 33405 Talence (France) – LPTC (p.labadie@epoc.u-bordeaux1.fr)
[4] CNRS, EPOC, UMR 5805 , 351 cours de la Libération, 33405 Talence (France) – LPTC (h.budzinski@epoc.u-bordeaux1.fr)
[5] LABERCA, ONIRIS Atlanpôle, Site de la Chantrerie, BP 50707 44307 NANTES Cedex 3 (France) (bruno.lebizec@oniris-nantes.fr)
[6] University of Aarhus, Frederiksborgvej 399, 4000 Roskilde (Denmark) (kvo@dmu.dk)
[7] IFREMER, Biogeochemistry and Ecotoxicology department, Laboratory of Organic Contaminants Biogeochemistry, rue de l'Ile d'Yeu, BP 21105, 44311 Nantes, Cedex 03 (France) (Jacek.Tronczynski@ifremer.fr)
Zone Atelier Bassin du Rhône

RÉSUMÉ

Drainant des régions relativement peuplées et industrialisées, le Rhône et ses affluents sont soumis à des pollutions diffuses et ponctuelles par une grande variété de substances chimiques. Les plus persistantes d'entre elles s'accumulent dans le biote aquatique, notamment les poissons. Nous présentons ici la synthèse de deux études récentes, qui constituent une première étape dans l'inventaire des contaminants d'intérêt émergent dans le bassin du Rhône. Les substances les plus fréquemment mesurées sont les polybromodiphényléthers (PBDE), comme dans beaucoup d'autres fleuves ; les hexabromocyclododécanes (HBCD) et perfluorés (PFC) devront faire l'objet d'études approfondies dans le futur.

ABSTRACT

Flowing through rather densely populated and industrialized areas, the Rhone river and its tributaries are subject to diffuse and localised releases of a wide variety of chemicals. The most persistent ones may accumulate in aquatic biota, in particular fish. We summarize here two recent studies, which are a first step in an updated knowledge of the contaminants of emerging concern in the Rhone and its tributaries. The most prevalent compounds in the Rhone catchment are polybromodiphenylethers (PBDEs), as in many other streams. Hexabromocyclododecanes (HBCDs) and perfluorinated compounds (PFCs) will have to be scrutinized more carefully in the future.

KEYWORDS

Fish, HBCD, PBDE, PFC, Rhone river.

1 INTRODUCTION

From the 1960s to 2001 and the signature of the Stockholm Convention on "persistent organic pollutants" (POPs), monitoring of chemicals in the environment has been focussed on chlorinated compounds. Interestingly, this international agreement also defined criteria for screening new POPs in terms of persistence, bioaccumulation, potential for long-range transport and toxicity UNEP (2001). From 2001 onwards a large number of such potential POPs, also named "chemicals of emerging concern" have been studied throughout the world. Some are considered for inclusion on priority substances lists or were added recently to the Stockholm convention annexes A (elimination) or B (restriction). Recently in Europe polybromodiphenylethers (PBDE) and the perfluorooctane sulfonate (PFOS) were added to the list of candidate priority substances in the context of the Water Framework Directive (WFD) implementation.

When the action plan on polychlorobiphenyls (PCBs) was adopted in France in 2008, several stakeholders agreed that it was a good opportunity to gather also some data on other less studied contaminants. Here we report on two studies carried out between 2008 and 2010 in the Rhone river catchment in this perspective:

(1) a first screening on a limited set of sites and a relatively large array of substances.

(2) a screening at a large spatial scale covering the Rhone catchment targeting two families of compounds, i.e. PBDEs and perfluorinated compounds (PFCs).

2 MATERIALS AND METHODS

2.1 Screening study (A)

Adult fish from 4 cyprinid species, namely the barbel (*Barbus barbus*), the common bream (*Abramis brama*), the silver bream (*Blicca bjoerkna*), and the chub (*Squalius cephalus*) were collected at three sites along the Rhone river. MTE is located about 90 km upstream Lyon, GDL is also located upstream Lyon, and downstream several industrial areas. BRE is located 40 km downstream Lyon.

Fish (mainly adults) were caught by a professional fisherman with nets between August 2008 and early January 2009. 50 samples, about half as pools of same size fish and half as individuals, were prepared according to Commission Directive 2006/13/EC, freeze-dried and transferred to the laboratories.

The studied compounds included 5 alkylphenols (AKP), i.e. 4-tert-octylphenol (OP), 4-nonylphenol (commercial mixture, NP), 4-nonylphenol-monoethoxylate (NP1EO), 4-nonylphenol-diethoxylate (NP2EO), 4-nonylphenoxyacetic acid (NP1EC), bisphenol A (BPA), 9 PBDEs: 28, 47, 99, 100, 153, 154, 183, 205 et 209, 14 perfluorinated compounds (PFC): perfluorobutanoic acid (PFBA); perfluoropentanoic acid (PFPA); perfluorohexanoïc acid (PFHxA); perfluoroheptanoic acid (PFHpA); perfluorooctanoic acid (PFOA); perfluorononanoic acid (PFNA); perfluorodecanoïc acid (PFDA); perfluoroundecanoïc acid (PFUnA); perfluorododecanoïc acid (PFDoA); Perfluorobutanesulfonate potassium (PFBS); Perfluorohexanesulfonate potassium (PFHxS); Perfluoroheptanesulfonate potassium (PFHpS); Perfluorooctanesulfonate potassium (PFOS); Perfluorodecanesulfonate potassium (PFDS); and 3 hexabromocyclododecanes (HBCD) isomers: α, β and γ.

2.2 Monitoring of PBDEs and PFCs at catchment scale (B)

93 sites were investigated in 2009-2010, yielding 823 samples (381 pools, 442 individuals) representing 27 fish species. The fishing protocol recommended to focus on two groups of species, according to their propensity to accumulate PCBs. 9 PBDE congeners (as above) and 17 PFCs (as above, plus acid perfluoro-octane sulfonic - PFOSA, acid perfluoro-tridecanoic – PFTrDA, and acid perfluoro-tetradecanoic - PFTeDA) were analysed. The data derived from this study are available through a web portal (http://www.rhone-mediterranee.eaufrance.fr/usages-et-pressions/pollution_PCB/basepcb/index.php).

3 RESULTS & DISCUSSION

3.1 Study A (3 sites on the Rhone river)

The detection frequency in pools, i.e. the ratio of the number of samples above the limit of quantification (LQ) to the number of samples analysed varied between 0 for PFCs having less than 8

carbon atoms, to 100% for PFDA, PFOS all PBDEs but congeners 183 and 209, NP and αHBCD. PFOA, BPA, γHBCD and PBDE 183 and 209 were quantified in less than 50% of pools, while PFNA, PFUnA, PFDS, βHBCD and OP had detection frequency between 50 and 90%. Detection frequencies in individuals were quite similar.

A clear up- to downstream gradient can be observed in individuals for PFCs and AKPs. For PBDEs and HBCDs, the medium site displays higher contamination levels than the downstream site, which has higher concentrations than the upstream one. The results differ slightly when considering pools, for instance the up- downstream gradient is more pronounced and linear for PBDEs when pools are analysed than in individuals.

In individuals, and according to $\delta^{13}C$ values, higher PBDEs concentrations are associated with higher proportions of carbon originating from sediment, however the correlation is weak, and the distribution of species among the 3 sites is uneven. Furthermore no relationships could be found with the trophic position ($\delta^{15}N$), for three reasons at least: variability of $\delta^{15}N$ values among individuals, similarity of the mean trophic positions of the 3 species, and specific effect of N sources such as domestic effluents (Anderson and Cabana, 2006), which provides depleted $\delta^{15}N$ values downstream.

3.2 Study B (catchment)

27 different species have been collected at 93 sites throughout the Rhone catchment; among these only 12 species were present at more than 10 sites, in numbers allowing a statistical treatment.

All PBDEs but the congener 205 are quantified in ≥90% of the 823 samples analysed. Highest concentrations were observed for the congeners 47 and 209. The species mostly prone to accumulate PBDEs are the European eel (*Anguilla anguilla*), the nase (*Chondrostoma nasus*) and the trout (*Salmo trutta fario*). Congener patterns differ among species: eel is the only species displaying important amounts of congener 100, and trout shows higher concentrations of congener 99. The congener 209 is more represented in eels, barbels and nases. These variations suggest differences in sources and PBDE metabolism.

Among PFCs, the perfluorooctane sulfonate (PFOS) is measured in 75 % of the 823 analysed samples. Other PFCs are less frequently measured: PFOSA (acid perfluoro-octane sulfonic) 13.2%, PFDA (acid perfluoro-decanoic) 17.3%, PFUnA (acid perfluoro-undecanoic) 9.2%, PFNA (acid perfluoro-nonanoic) 7.2%. Other PFCs are measurable in ≤5% of the samples. The spatial distribution of the PFCs other than PFOS suggest local sources, in relation with either production or uses of these compounds. When considering the sum of concentrations of 17 PFC or the PFOS alone, the species most prone to accumulate are the gudgeon, the roach, and to a lesser extent the European eel and the barbel.

4 SUMMARY AND PERSPECTIVES

Flowing through rather densely populated and industrialized areas, the Rhone river and its tributaries are subject to diffuse and localised releases of a wide variety of chemicals. The most persistent ones may accumulate in aquatic biota, in particular fish, raising concerns about the ecotoxicological and health impacts of these chemicals. The studies that we summarized here are a first step in an updated knowledge of the contaminants of emerging concern in the Rhone and its tributaries. The most prevalent compounds in the Rhone catchment are PBDEs, as in many other streams, but HBCDs and PFCs will have to be scrutinized more carefully in the future. Further research will have to look for guidelines and accumulation processes model development.

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