

Introduction and objectives

The European Water Framework Directive (WFD) aims to achieve and ensure a good quality status of water in each Member State. Environmental Quality Standards (EQSs) have been set in biota for some substances (Directive 2008/105/EC). This is the case of mercury, hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD). Moreover the recent Directive 2013/39/EU adds other substances to that list, including PAHs (benzo-a-pyrene and fluoranthene).

To answer these recommendations we developed methods to measure the concentration of these pollutants in freshwater biota sampled in Walloon Rivers. Four fish species (*Leuciscus cephalus*, *Abramis brama*, *Cottus gobio*, *Barbatula barbatula*) and benthic macroinvertebrates (crustaceans or molluscs) were chosen for their interest as sentinel species. During the years 2013-2014, thirty four sites distributed in 3 hydrographic districts and corresponding to surveillance monitoring sites defined for the WFD were sampled for these organisms everytime they were present. Results are discussed for fish sampled from 11 sites and invertebrates from 19 sites. Other samples are currently analysed.

In addition, fifteen other sites were visited without finding the sentinel species and no results could be obtained. To overcome this problem, a caging technique with the crustacean *Gammarus pulex* is currently being developed. A preliminary experiment was conducted.



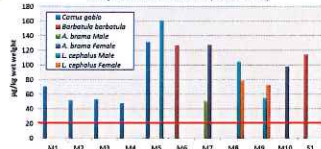
Results

Mercury

EQS = 20 µg/kg wet weight

Mercury (µg/kg wet weight)	Mean ± s.d.	Min.	Max.
<i>L. cephalus</i> (n=14)	96 ± 49,8	34,4	200
<i>A. brama</i> (n=5)	106,6 ± 40,9	51	166
<i>C. gobio</i> (n=6 pools)	71,1 ± 31,2	48	131,5
<i>B. barbatula</i> (n=2 pools)	120,8 ± 8,84	114,2	127

Mercury concentration (µg/kg wet weight) in fish muscles sampled in Walloon rivers (2013 - 2014)



- Mercury concentrations in fish are above the EQS in all sampling sites ;
- Highest concentrations:** muscles of male chubs from one Meuse basin site (One sample from M5 site, 200µg/kg wet weight. Mean concentration in chubs from M5 = 161µg/kg wet weight).

HCBD - HCB

EQS - HCB = 10 µg/kg wet weight
EQS - HCBD = 55 µg/kg wet weight

- Results obtained for the same sampling sites as for mercury;
- HCB and HCBD concentrations in fish samples are always below the LOQs (2 µg/kg wet weight).

→ Concentrations are always below the EQSs

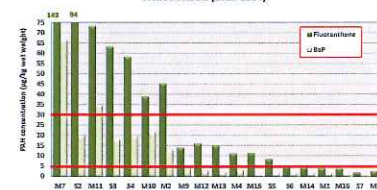
Benzo-a-pyrene and fluoranthene

Fluoranthene (µg/kg wet weight)	Mean ± s.d.	Min.	Max.
Crustaceans (n=15)	28,4 ± 30,0	2,5	93,6
Molluscs (n=4)	47,1 ± 66,4	1,9	143,3

Benzo-a-pyrene (µg/kg wet weight)	Mean ± s.d.	Min.	Max.
Crustaceans (n=15)	8,2 ± 10,3	<LOQ	34,5
Molluscs (n=4)	22,6 ± 30,9	0,6	66,6

PAHs concentrations in fish are always below the EQSs because these compound are quickly metabolized
→ EQSs established for invertebrates

PAHs concentrations (µg/kg wet weight) in invertebrates from Walloon rivers (2013-2014)



EQS - BaP = 5 µg/kg wet weight
EQS - Fluoranthene = 30 µg/kg wet weight

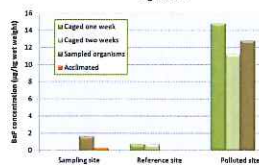
- Concentrations are above the EQS for approximately 40% of the stations : 7 sites out of 19 for fluoranthene and 8 sites out of 19 for benzo-a-pyrene;
- Highest BaP concentrations:** molluscs from one Meuse basin site (M7: 66,6 µg/kg wet weight) and crustaceans from one Meuse basin site (M11: 34,5 µg/kg wet weight).
- Highest Fluoranthene concentrations:** molluscs from M7 site (143,3 µg/kg wet weight) and crustaceans from one Scheidt basin site (S2: 93,6 µg/kg wet weight).

Caging gammarids

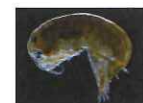
Gammarids coming from a clean sampling site were acclimatized for two weeks in the laboratory and caged either in one reference site or in one polluted site. The experiment lasted one or two weeks to establish the time to equilibrium. Benzo-a-pyrene and fluoranthene were searched in these organisms after caging.



Benzo-a-Pyrene concentrations in organisms from sampling site, reference site, polluted site and caged organisms



Fluoranthene concentrations in organisms from sampling site, reference site, polluted site and caged organisms



- Organisms caged in polluted site are more contaminated than in reference site and concentrations are similar to those observed in organisms living in these sites;
- There are no important differences of contamination after one or two weeks of caging → one week caging should be enough to allow the organisms to equilibrate with the new environmental conditions.

- Fluoranthene concentrations are always higher than BaP concentrations;
- A decrease of BaP concentration is observed after 2 weeks acclimatization;

Conclusion

- Mercury concentrations in fish from Walloon rivers are always high but HCB and HCBD concentrations are always lower than the LOQs. These results are similar to those obtained elsewhere in Europe;
- Contamination is different according to sites and some places are more contaminated than others. Moreover one sampling site can be contaminated with some pollutants but not all of them;
- In the different basins, the most contaminated sites are usually located on the biggest rivers and/or the sites located in more industrialized regions. Small rivers are generally less contaminated;
- Results obtained for caged gammarids show that PAHs concentrations reach the equilibrium after one week caging. In the future, this method could be adapted to obtain results in rivers where crustaceans are absent. Further experiments are currently on-going.