PERFLUORINATED ALKYL ACIDS IN BIVALVES, WATER, AND SEDIMENTS OF THE PO RIVER DELTA (ADRIATIC SEA)

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Introduction

The river Po (Northern Italy) is the longest river in Italy (652 km) and it flows across the Pianura Padana eastward with a drainage area of 74,000 km² (about one fourth of the whole Italian surface) and more than 16 million people lived in the whole basin, nearly one third of the Italian population. The Po basin generates nearly 40% of the Italian national GDP through intensive industry and other economic activities. Among the industrial activities, an important fluoropolymer production plant is located in Po basin and it is the most significant source of PFOA in the basin[1]. Our previous study[2] showed that the PFAS load from Po (about 4.1 t/y) still remains a significant contribution to the Adriatic Sea, even if PFOA load from river Po (1.7 t/y[2]) is significantly reduced respect to previous data (9.5 t/y[1]).

The farming of mollusks is extensively developed in the lagoons of the Po Delta. Consequently, the bioaccumulation of these compounds in the aquatic trophic webs poses concern about the risks for end consumers, including humans.

In this study, the concentrations of perfluorinated carboxylates (PFCA, from C5 to C10) and perfluorinated sulfonates (PFSA, C4 and C8) was determined in water, sediment, and in biota tissues of the mussel *Mytilus galloprovincialis* and the clam *Venerupis philippinarum* sampled in the Po Delta. The bioconcentration factors (BCFs) were also evaluated in bivalves. Being the bivalve species studied largely consumed in Italy, the Tolerable Daily Intake (TDI) was calculated in order to evaluate the risk for humans.

Materials and methods

Water, sediment (3 replicates per site) and bivalve samples (*Mytilus galloprovincialis*, n=3 pools of 5 specimens, homogenized whole body; *Venerupis philippinarum*, n=3 pools of 5 specimens, homogenized whole body) were collected in three sampling sites of the Sacca di Goro Lagoon (44°47'-44°49'N, 12°17'-12°20'E), located in the southern part of the Po Delta, in April 2011. The three sampling sites are subjected to different pollution pressures: 1. a site is located in the Eastern part of the lagoon (EST) where the human impact is high and where there is a direct influence of river Po waters; 2. the bivalve reproduction site (NURC) is where the lagoon waters merge the Adriatic seawaters and it is characterized by low human impact; 3. a site is located in front of Punta Volano (VOL) and it receives waters from cultivated fields and from canals which drain little urbanized areas, therefore it shows a moderate human impact.

Analysis of perfluoroalkyl acids (PFAAs: PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFBS, PFHxS, PFOS) in water samples was carried out by LC-MS/MS coupled with on-line SPE[3]. LODs and LOQs of this on-line SPE method ranged from 0.2 to 5.0 ng/L and from 1 to 20 ng/L respectively. Sediment and biota samples were extracted with ultrasonic assistance by a ACN/H_2O mixture enhanced by salting out and acidified after volume reduction. The extracts were on-line cleaned up by on-line turbulent flow chromatography before LC-MS/MS analysis[4]. LODs and LOQs ranged from 0.03 to 0.3 ng/g wet wt and from 0.1 to 0.9 ng/g wet wt, respectively.

Results and discussion

Concentrations of PFOA and PFOS in water (PFOA: 12-15 ng/L; PFOS: 4-5 ng/L) and sediment (PFOA: 0.23±0.01 - 0.96±0.04 ng/g dry wt; PFOS: <0.03 - 0.31±0.03 ng/g dry wt) were similar to the typical environmental concentrations of the industrialized countries (Figure 1). No significant differences were detected in PFAA concentrations in the three sampling sites. Short chain PFCAs (PFPeA = 5-8 ng/L; PFHxA = 3-4 ng/L) were detected only in water samples.

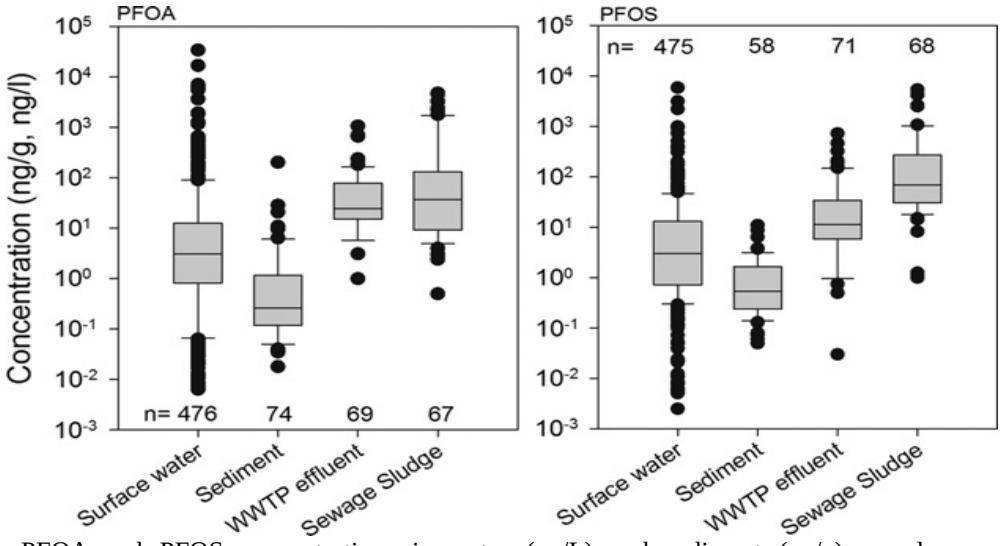

Figure 1: PFOA and PFOS concentrations in water (ng/L) and sediment (ng/g) samples compared to industrialized areas (from Zareitalabad et al., 2013[5], modified).

The PFAA contamination patterns in clams and mussels do not reflect that determined in water and sediment. PFPeA, PFHxA, PFBS and PFHxS were not detected in the bivalve samples. In mussels, the PFAAs ranged from 0.10 to 0.41 ng/g wet wt; PFOA and PFOS were the dominant homologue in clams with concentrations ranging from 2.2 to 4.5 ng/g wet wt and from 0.59 to 1.13 ng/g wet wt for PFOA and PFOS, respectively (Table 1).
The PFDoDA concentrations in mussel tissues were higher than the other PFAA; PFOS was not detected in the river estuary site (NURC), where water mainly comes from the Adriatic Sea and the human impact is low. Interestingly, higher PFOA levels where detected in mussel tissues where the human impacts exist (EST). The other PFAA, namely PFPeA, PFHxA, PFHpA, PFNA, PFBS, and PFHxS were lower than the detection limits in all samples.
The PFOA was the most abundant PFAA in clam and its concentrations were much higher than PFOS and PFDA, in all sites. PFHpA and PFNA were at detectable levels and PFHxA, PFHpA, PFNA, PFBS, PFHxS always lower than LODs (Table 1).
The concentration of ΣPFAAs was much higher in the clam than in the mussel (Figure 2). The lower concentrations in mussels might be explained by the elimination of some PFAA through gill respiration, as already reported for other gill breathing organisms: a high breathing/filtration rate may affect the PFAA bioaccumulation.
The concentrations of PFAA detected in mussels were of the same order of magnitude than those measured in European and Asiatic countries (exceptions: Portugal, Japan)[6]. Regarding the clam, PFAA levels were similar to those detected in polluted areas (Japan, Korea) and higher respect to the pristine Arctic[6]. The pattern was similar to that found in clam from Japan, being PFOA the most abundant PFAA.
The BCF values for PFOA calculated from the dataset of the present study and from literature data (Table 1) span three orders of magnitude: it must be highlighted that generally the highest BCF values correspond to the lowest PFOA concentrations in water and vice versa. This relationship is linked to the concentration dependency of the bioaccumulation of PFAA which was modeled by Liu et al. (2011)[7], probably because these compounds accumulate into protein-rich compartments.

Conclusions

Considering the Italian average daily consumption of fresh and frozen shellfish (4.6 g/person) and the Tolerable Daily Intake (1.5 µg/kg b.w. for PFOA and 150 ng/kg b.w. for PFOS[13]) no health risk has been envisaged arising from dietary exposure to PFOS and PFOA at levels found in mollusk collected in the Sacca di Goro Lagoon of Po Delta.
There is no direct correlation between the PFAA concentrations in soft tissue of bivalve and water but BCFs increase as water concentrations decrease. This evidence suggests that special attention should be taken when bivalves are used for environmental quality monitoring of perfluorinated compounds.

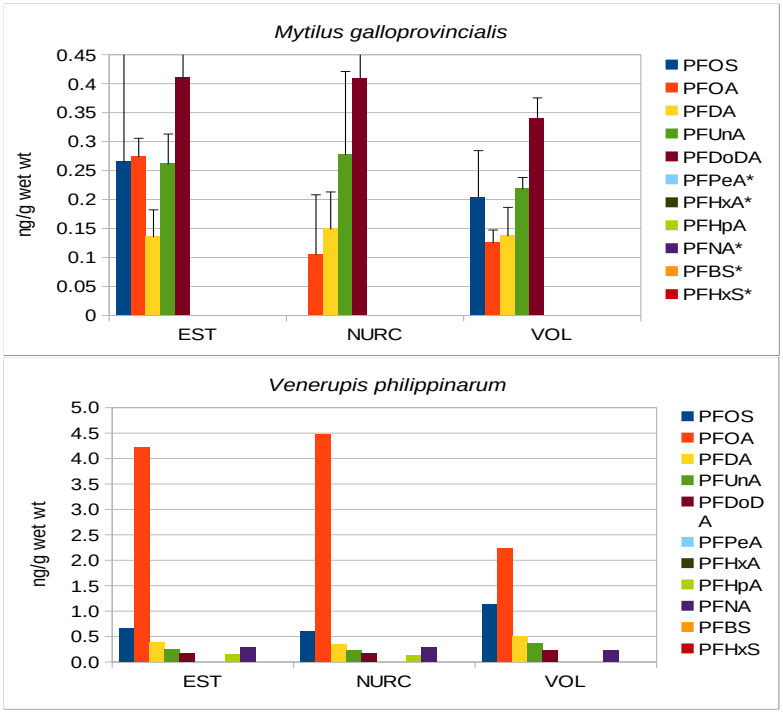

Figure 2: Concentrations (ng/g wet wt) of PFAAs in the mussel (a) and clam (b) and comparisons.

Table 1: Concentrations of PFOA in bivalve tissues (ng/g wet wt) and water (ng/L), and BCF values.

	site	soft tissue	water	BCF	References
Mussel	VOL	0.12	15	8	present study
Mussel	NURC	0.10	12	9	present study
Mussel	EST	0.27	12	22	present study
Mussel		0.94	10	93	[8]
Mussel (*D. polymorpha*)		2.5	10	262	[9]
Mussel		9.5	0.6	14844	[12]
Clam	EST	4.2	12	346	present study
Clam	NURC	4.5	12	364	present study
Clam	VOL	2.2	12	184	present study
Venus clam		15	1.5[10]	9932	[11]
Clam		7.5	0.6	11719	[12]

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Bacino del Po e nei principali bacini fluviali italiani". A warm thank to Carlo Zaghi (MATTM) for the support in promoting this study.

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