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Perfluorinated compounds: Levels, trophic web enrichments and human dietary intakes in transitional water ecosystems

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ABSTRACT

The results of a study on levels of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), analyzed in terms of HPLC-ESI-MS in water, sediment, macrophyte, bivalve, crustacean and fish samples, are reported here. The aim of the research is to define, for the first time, PFOA/S levels in a heavily human-stressed transitional water ecosystem (Orbetello lagoon, Italy) and evaluate trophic web enrichments and human dietary intakes. The results obtained show that: (i) levels significantly higher than those reported in the literature were found in mussels, clams and crabs; (ii) the river is a significant pollution source; (iii) although absolute levels are relatively low, macroalgae proliferation contributes to redistribute pollutants from river-affected areas throughout the entire lagoon basin; (iv) to the best of our current knowledge, water-filtering species considered in this study are the most exposed to PFOA/S pollution; (v) human daily dietary intakes of PFOA/S through Slow Food-endorsed product consumption are below maximum tolerable levels suggested by the EFSA.

1. Introduction

Perfluorinated organic compounds (PFCs) are emergent persistent organic pollutants widely used for industrial and commercial applications including adhesives, agrochemicals, fire-fighting retardants, foams propellants, food packaging, lubricants, medicines, paints, polishes, refrigerants, and surfactant production (Renner, 2001). In particular, fire-fighting use for accident prevention during high-risk military procedures, routine fire-fighting training exercises and airport activities are the main direct sources of pollution of soil, fresh water and groundwater (Moody and Field, 2000), but leaching from discarded food packaging and runoff from discarded painted objects also produce significant indirect emissions (Renzi, 2012 and citations therein).

These emission sources release significant quantities of PFCs into the aquatic environment. In Europe for the year 2007, PFOS and PFOA discharges along the entire European river network to coastal areas have been estimated to be around 20 and 30 tons/year, respectively (Pistocchi and Loos, 2009).

Although in widespread use for a variety of purposes, these chemicals are hazardous substances which could affect the health of ecosystems and organisms due to their endocrine-disrupting activity, of which relatively little is described in the literature (Richardson and Ternes, 2005; Renzi, 2012 and citations therein). Recently, some studies documented PFCs in wildlife tissues (Kannan et al., 2002; Olivero-Verbel et al., 2006; Perra et al., 2010) and human body fluid samples (Yeung et al., 2006; Guerranti et al., 2013), suggesting a significant wide-ranging diffusion in the environment and a concrete exposure risk for human populations (Midasch et al., 2006).

A general lack of knowledge on environmental levels and bio-enrichment dynamics is reported for transitional water ecosystems as well as river effluents or lagoons.

This study, carried out in the Orbetello lagoon (Italy), aims to: (i) provide data on PFC levels in a large number of different environmental and biological matrices; (ii) compare observed levels with values reported in the literature for other aquatic ecosystems both in Europe and worldwide; (iii) evaluate the occurrence of enrichments throughout the lagoon trophic web; (iv) evaluate daily dietary intakes for humans related to the consumption of Slow Food-endorsed products from the lagoon.

2. Materials and methods

2.1. PFC physical–chemical features

PFCs are anionic fluorine-containing surfactants soluble in both water and oil and characterized by a half-life of more than two months in water and more than six months in sediments/soils

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(UNECE, 1998). Their physical-chemical properties favor long-range transport. Atmospheric conveyance of volatile precursor compounds and ocean currents have an important role in the global distribution of PFCs (Simcik, 2005a,b; Prevedouros et al., 2006), which are more volatile than chlorine or bromine analogues. Perfluorooctanoic acid (PFOA) and perfluoroctanesulfonic acid (PFOS) are the specific PFCs considered in this study; their physical-chemical features are summarized in Table 1. The carboxylic acid surfactant PFOA is much more volatile and soluble in water than PFOS and is measurable in environmental matrices (Corsolini et al., 2012; Senthilkumar et al., 2007), while PFOS is found predominantly in biota (Senthilkumar et al., 2007).

2.2. Study area

The Orbetello coastal lagoon (Central Tyrrhenian sea, Fig. 1) was selected for this study on the basis of general scientific knowledge developed in previous research (Renzi et al., 2013). Its principal meteorological, geomorphologic, hydrological and ecological characteristics are summarized in Table 2. The Albegna river ensures freshwater inputs throughout the Fibbia canal (W-basin) and represents a source of nutrients (ARPAT, 2007a,b) and pollutants due to human activity (Renzi, 2007; Specchiulli et al., 2008; Perra et al., 2009; Renzi et al., 2009, 2013) for the lagoon ecosystem. Direct fishing and aquaculture are important commercial resources in this ecosystem, principally based on eel (*Anguilla anguilla* L., 1758), sea bass (*Dicentrarchus labrax*), gilthead sea bream (*Sparus auratus* L., 1758), and sole (*Solea vulgaris*).

2.3. Experimental design

PFOA/S levels were measured in water, sediment, and biota collected in six sampling stations located in the Orbetello lagoon (Fig. 1). Organisms living at different trophic levels were collected, including primary producers, herbivores, filter feeders, and carnivores. Sampled species were: macrophytes (*Alsidium corallinum*, *Chaetomorpha linum*, *Cymodocea nodosa*, *Ruppia cirrhosa*), bivalves (*Mytilus galloprovincialis*, *Ruditapes decussatus*), crustaceans (*Palaemon serratus*, *Carcinus aestuarii*), and fish (*Parablennius* sp., *Zosterisessor ophiocephalus*, *Atherina* sp., *Gobius niger*). Samples were sized to reduce Type *I* and Type *II* errors according to a logical model (Underwood, 1994; Underwood and Chapman, 2003; Benedetti-Cecchi, 2004) based on a nested hierarchical design developed on three fixed *versus a priori* randomly defined factors: matrix (three levels, fixed), internal spatial variability (six levels, fixed), sampling replicates (three, random). To reduce sampling error, the geographical locations of sampling replicates were randomly extracted from a squared subsample grid of $1 \times 1\ km^2$ (Cochran, 1977), and extracted coordinates were localized *in situ* using a Global Positioning System (Garmin, mod. *e*-trex legend). The number of sampling replicates varied depending on the matrix considered. Abiotic matrices (water and sediments) and macrophytes were collected in triplicate and analyzed separately to include low-range spatial fluctuations, while animal species were sampled in statistical replicates considered representative of the entire lagoon population. As far as the ecological behavior of each species is concerned, not all of the six sites were sampled. To obtain sufficient quantities of tissues, analytical pools were prepared mixing equal wet weight of corresponding anatomical parts excised from ten organisms of the same species, obtaining a real $n = 30$ per each of the six selected sampling stations. Variability due to sediment grain size was *a priori* excluded: sediments characterized by a high silt content fluctuating within a narrow range (80–90% d.w.) were considered. It is well known that in water, POP levels tend to increase with body size as a function of exposure time; to reduce age-dependant variability, analyses were performed on a narrow-range distribution of body length (Renzi et al., 2012). Aquatic exemplars were sampled using movable trap nets (*bertovelli*) set within each sampling area in May 2008 to standardize seasonal-based temporal variability of pollution, biological phenomena linked to life cycle stages and sexual activity.

2.4. Sampling and laboratory pre-treatment of matrices

Water was sampled 5 cm under the surface and transferred after *in situ* filtration into a pre-cleaned HDPE polypropylene bottle

Table 1
Physical-chemical characteristics of studied molecules. Substance identification (extended names and international classification numbers), principal molecular properties, and related risks of PFOA (perfluorooctanoic acid perfluorooctanoate) and PFOS (perfluoroctanesulfonic acid) are summarized in table. Specific references: PFOA records were extracted from the GESTIS Substance Database from the IFA (last access on 5th November, 2008), Prevedouros et al., 2006.

	PFOA	PFOS
Extended name	Perfluorooctanoic acid	Perfluoroctanesulfonic acid
Other names	Perfluorooctanoate Perfluorocaprylic acid FC-143 F-*n*-octanoic acid	1-Perfluorooctanesulfonic acid Heptadecafluoro-1-octanesulfonic acid Perfluoro-n-octanesulfonic acid
Substance identification		
CAS numb	335-67-1	1763-23-1
Pubchem	9554	74483
EC number	206-397-9	217-179-8
Molecular properties		
Molecular formula	$C_8HF_{15}O_2$	$C_8HF_{17}O_3S$
Molecular mass	414.07 g mol^{-1}	500.13 g mol^{-1}
Boiling point	189–192 °C	133 °C (6 torr)
Appearance (25 C, 100 kPa)	Colorless liquid	White powder
Vapor pressure	4.2 Pa (25 °C)	3.31×10^{-4} Pa (20 °C)
Melting point	40–50 °C	>400 °C
Solubility in water	3400 mg L^{-1}	519 mg L^{-1} (20 ± 0.5 °C) 680 mg L^{-1} (24–25 °C)
Solubility in other solvents	Polar organic solvents	56 mg L^{-1} (octanol)
Acidity (p*K*a)	2–3	Calculated value of −3.27
Related risks		
S-phrases	S36, S37, S39	S61
R-phrases	R22, R34, R52/53	R61, R20/21, R40, R48/25, R64, R51/53