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Occurrence and sources of perfluoroalkyl acids in Italian river basins

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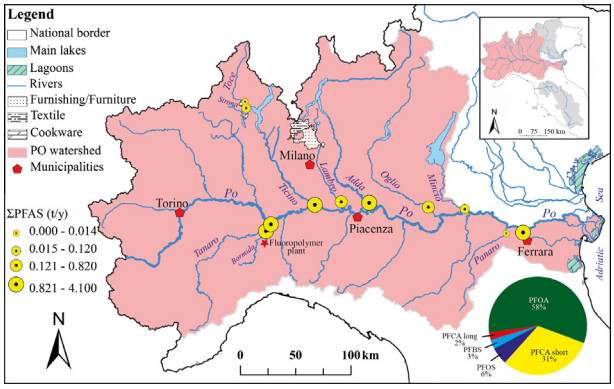
HIGHLIGHTS

- PFAA concentrations and loads of the main Italian river basins, 40% of Italian area.
- Total concentrations of PFAA ranged from < LOD to 8 μg L^{-1}.
- The most discharged compounds are PFBS (39%) and PFOA (32%).
- Urban load (0.09 t y^{-1}) is 1% of the total PFAA load to sea (7.9 t y^{-1}).
- The main PFAA sources of Italy are two chemical plants (57% of the total load).

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents a survey on the occurrence and sources of 11 perfluoroalkyl acids (PFAA) in the main river basins in Italy, covering about 40% of the Italian surface area and 45% of the Italian population. Total concentrations of PFAA ranged from < LOD to 8 μg L^{-1}, the highest concentrations being measured in the rivers impacted by industrial discharges. Among the rivers directly flowing into the sea, Brenta, Po and Arno present significant concentrations, while concentrations in Tevere and Adige, which are not impacted by relevant industrial activities, are almost all below the detection limits.

The total estimated PFAA load of the five rivers was 7.5 t y^{-1} with the following percentage distribution: 39% PFBS, 32% PFOA, 22% short chain perfluorocarboxylic acids (PFCA), 6% PFOS and 1% long chain PFCA. PFOA and PFOS loads, evaluated in the present work, represent 10% and 2% of the estimated European loads, respectively.

In Italy the most important sources of PFAA are two chemical plants which produce fluorinated polymers and intermediates, sited in the basin of rivers Po and Brenta, respectively, whose overall emission represents 57% of the total estimated PFAA load. Both rivers flow into the Adriatic Sea, raising concern for the marine ecosystem also because a significant PFOS load (0.3 t y^{-1}) is still present.

Among the remaining activities, tanneries and textile industries are relevant sources of respectively PFBS and PFOA, together with short chain PFCA. As an example, the total PFAA load (0.12 t y^{-1}) from the textile district of Prato is equivalent to the estimated domestic emission of the whole population in all the studied basins.

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1. Introduction

Because of their peculiar physical and chemical characteristics, perfluoroalkyl substances (PFAS) find wide application in several industrial processes and products, such as surface treatment of textiles and paper, building paints, cosmetics, insecticide formulations, firefighting foams, and the production of fluoropolymer (Kissa, 2001; Prevedouros et al., 2006; Buck et al., 2011). However, their characteristics, such as resistance to hydrolysis, photolysis, microbial degradation (Giesy and Kannan, 2001; Prevedouros et al., 2006) make these substances highly persistent and widespread in all environmental compartments. Water is the major reservoir of these compounds in the environment, as well as the most important medium for their transport (Prevedouros et al., 2006; Mc Lachlan et al., 2007).

PFAS include thousands of chemicals but environmental studies mainly concentrated on perfluoroalkyl acids (PFAA), such as perfluoroalkylsulphonic acids (PFSA) and perfluoroalkylcarboxylic acids (PFCA). PFSA and PFCA are low molecular weight surfactants, consisting of homologous series of completely fluorinated carbon chains. The two PFAA, most commonly used and found in the environment, are perfluorooctanesulphonate (PFOS) and perfluorooctanoate (PFOA). They have been widely employed in different industrial processes (Kissa, 2001; Prevedouros et al., 2006). Their persistence in the environment together with their bioaccumulation in the trophic chain raised concern about the risks for consumers, including humans, so that European Commission recently included PFOS in the list of priority hazardous substances under the Water Framework Directive (WFD), setting an Environmental Quality Standard (EQS) of 0.65 ng L^{-1} for freshwater (EC, 2013). At the moment for PFOA, no limits have been established in the aquatic environment, but only a provisional threshold for drinking waters proposed by US Environmental Protection Agency (EPA) of 0.4 μg L^{-1} (EPA, 2009). The regulatory restrictions on the use of PFOS and PFOA (EC, 2006; EPA, 2006) induced the major fluorochemical producers to search substitutes for these compounds, especially among homologues with shorter chain lengths (Wang et al., 2013).

Manufacturing facilities of fluorochemicals are the greatest point sources of PFAS (Prevedouros et al., 2006; Davis et al., 2007) while emissions of municipal and industrial wastewater treatment plant (WWTP) are less relevant (Boulanger et al., 2005; Prevedouros et al., 2006; Schultz et al., 2006; Sinclair and Kannan, 2006).

The first comprehensive study evaluating the concentrations and loads of PFAA in main European rivers was carried out in the framework of the EU project PERFORCE (Mc Lachlan et al., 2007); this paper was followed over the years by several studies investigating their occurrence in surface waters both along big rivers (Ahrens et al., 2009; Loos et al., 2010; Möller et al., 2010) and at regional scale (Ericson et al., 2008; Clara et al., 2009; Rostkowski et al., 2009; Kwadijk et al., 2010; Sanchez-Avila et al., 2010; Muller et al., 2011; Dufkova et al., 2012). Furthermore, a pan-European screening of 122 water samples coming from several streams and rivers was also carried out (Loos et al., 2009). Published data about PFAA occurrence in Italian waters are currently available (Mc Lachlan et al., 2007; Loos et al., 2007, 2008; Castiglioni et al., 2014). The first study measured four PFCA at River Po basin closure, pointing out that Po had the highest concentration of PFOA in Europe (Mc Lachlan et al., 2007). The second study, which determined four PFCA and PFOS along river Po and its tributaries, identified a fluoropolymer plant, sited in river Tanaro basin, as the main PFOA source in river Po basin (Loos et al., 2008).

Our work is the first comprehensive study carried out on the main river basins in Italy, covering more than 40% of the national surface area. We obtained a map of occurrence and emissions of PFAA in the main Italian rivers and highlighted hot spots correlated with specific sources and industrial emissions. Streams and rivers, which drain areas of specific industrial districts, such as textile, tannery, furnishing and household districts, were also sampled.

The collected data allowed us to evaluate the uses and emissions of different PFAA homologues, including molecules that could be potential substitutes of PFOA and PFOS in industrial processes.

From the average concentrations measured at the basin closure, the PFAA loads discharged by rivers into the sea, which is the last receptor of these extremely persistent molecules, have been estimated.

2. Material and methods

2.1. Study areas

Five river basins of the longest Italian rivers which cover the most industrialised areas of Italy were surveyed (Table 1).

River Adige, located in north-eastern Italy, is the second longest river in Italy and flows into the Adriatic Sea (Fig. 1). Its basin is one of the least densely populated regions of Italy (the most populated city is Verona with 258 893 residents) and the main economic activity is agriculture. The last tributary is the river Alpone-Chiampo which flows through the most important tannery district in Italy (Arzignano and Valle del Chiampo).

River Brenta, originating from the lakes of Levico and Caldonazzo (Trentino region), flows into the northern Adriatic Sea, just south of the lagoon of Venezia (Fig. 1). The prevailing activity in its basin is agriculture but a cluster of SME is spread along its catchment. Just before the mouth, it receives the waters of River Bacchiglione, which drains waters from cities of Vicenza (113 352 residents) and Padova (210 914 residents), and River Fratta-Gorzone, which collects treated wastewaters from a textile district, a tannery district and a fluorochemical factory.

River Po is the longest river in Italy (652 km) and has the greatest discharge (1470 $m^3 s^{-1}$). It flows across the entire northern Italy and it has a drainage area of 74 000 km^2, (about one fourth of the whole Italian surface), of which 45 000 km^2 are in mountainous environments and 29 000 km^2 on the plain (Fig. 2).

The river flows through many important Italian towns, including Torino (901 286 residents), Piacenza (102 225 residents) and Ferrara (130 837 residents), but its catchment, which includes 141 tributaries, covers the main industrialised and populated areas of the country, such as the metropolitan area of Milano (4.4 million inhabitants). More than 16 million people live in the whole basin, nearly one third of the Italian population. The Po basin generates nearly 40% of the Italian Gross Domestic Product by intensive industry and other economic activities. Industries are concentrated in the urban areas of Torino, Milano, Brescia, Mantova and Ferrara with a long-standing tradition in automobile, motor and mechanics manufacturing as well as fine and bulk chemical production. The moist and fertile flood plain is exploited mainly for agriculture.

River Tevere rises in the Apennine Mountains in central Italy and, after a course in a generally southern direction, flows into the Tyrrhenian Sea soon after having crossed Roma, the most populated city of Italy (2 651 040 residents) (Fig. 3). The Tevere valley is partly hilly and partly a fertile plain where agriculture, crafts and animal husbandry are the main sources of income. Industrial development in the region is limited to the areas south of Roma outside the Tevere basin.

River Arno originates on Mount Falterona, (Apennines Mountains, central Italy), passes near Arezzo (98 537 residents), through Firenze (365 539 residents), Empoli (47 912 residents) and Pisa (86 591 residents), and flows into the Tyrrhenian Sea at Marina