PERFLUORINATED COMPOUNDS IN WASTEWATERS, SURFACE WATERS AND TAP WATERS IN TUSCANY (ITALY)

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Introduction:

Perfluorinated alkyl acids (PFAA) are a group of compounds that have been manufactured and widely used in multiple industrial processes since the 1950's^{1,2}. PFAAs have surfactant properties and have been used to coat solid materials such as paper and packaging, in making products water- and oil repellent, and impart stain resistance. They have been also used in fire-fighting foams and textile, and in many other products.

The two compounds more discussed in the PFAA group are perfluorooctanesulphonic acid (PFOS) and perfluorooctanoic acid (PFOA) which are known as PBT (persistent, bioaccumulative, toxic), which means that they are chronically toxic, persistent and bioaccumulative.

The environmental distribution of PFOS and PFOA has been extensively studied and well documented, in particular, various studies have evidenced their occurrence in surface and ground waters^{3,4,5,6,7}, in air^{8,9}, in biota^{10,11}, and in remote areas^{12,13}. In fact, due to their characteristics, such as their high water solubility and persistence, PFAAs are mobile in soil, are prone to leaching into groundwater and can travel large distances.

PFAAs pose serious risks to human health. There are various well-documented health effects associated with exposure to PFAAs, which include high cholesterol, thyroid disease, weight gain, and reproductive effects.

Thus, general population is exposed to different levels of PFAA from various sources, as ingestion of drinking waters and consumption of fish from contaminated sites. For this reason, it is fundamental to evaluate the occurrence and level of concentrations of these contaminants in different water bodies, drinking water and wastewaters in Tuscany (Italy) as well as to estimate human exposure and potential for bioaccumulation.

Materials and methods:

River waters were collected across the Tuscany region (Italy) in areas of likely recreational and/or sustenance fishing activities. Tap water samples were also collected in Tuscany cities with different equivalent inhabitants to verify the presence of perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorodecanoic acid (PFDA) and perfluorooctanesulphonate (PFOS). Wastewater samples were also analyzed considering that these contaminants are resistant to many, if not most, traditional water treatment processes.

All standards were purchased from Wellington Laboratories (Canada). Samples were spiked with 1,2,3,4 - ${}^{13}C_4PFOA$ and 1,2,3,4 - ${}^{13}C_4PFOS$ as internal standards and passed through a SPE cartridge (Oasis, Waters). The extracts were reduced in volume and analyzed by using a high performance liquid chromatography (HPLC) with electrospray ionization (ESI) tandem mass spectrometry. Concentrations were evaluated in comparison to an external calibration curve. Recoveries standards were between 83 and 111% for 1,2,3,4 - ${}^{13}C_4PFOA$ and 88 and

113% for 1,2,3,4 $-{}^{13}C_4PFOS$. The repeatability and reproducibility were performed in triplicate. LOD was evaluated and was below 1 ng/L and LOQ was between 1-18 ng/L.

Results and discussion:

The effluents of industrial waste waters showed higher concentrations of PFAAs in residential wastes, ranging up to 0.13 μ g/L. PFOA was the most abundant compound in the investigated wastewater treatment plants (WWTPs), with higher concentrations in the WWTP treating industrial wastes from textile manufactures in Tuscany. A relative high abundance of PFOA was followed by PFHpA and PFNA. The presence of PFHpA, which was not present in the influent, could be related to degradations processes or plastic contamination in the plant.

PFOA was determined in all waterbodies, not only close to industrialized area but also in non-industrialized areas, showing that these organic compounds undergo long-range transportation in the environment. Mean concentration of PFAAs in river water samples ranged from LOD to 954 ng/L, with PFOA as the dominant compound. The concentrations of PFOA were highest in the downstream of WWTPs, with concentrations similar to those determined in other Italian river waters¹⁴. PFOS concentrations were found only in few cases and at concentration levels about 10 times lower than PFOA. In fact, even if the use of PFOS and PFOA has declined in recent years, they have been replaced by other highly fluorinated substances, such as fluorotelomer alcohols, which can slowly degrade to PFOA.

Analysis of tap waters showed different levels of concentration in the residential areas, with concentrations strongly related to proximity of industrial areas.

However, all samples were below the 40 ng/L indicated as safe limit for PFOA, calculated according to the EFSA Tolerable Daily Intake and the World Health Organization conversion rules¹⁵. However, it should be taken into consideration that the human could be exposed to these contaminants also through food ingestion and contaminated consumable items.

Data showed a ubiquitous distribution of PFAAs in the water environments in Tuscany, with higher concentrations in the industrial areas. The different concentrations found in the effluents of WWTPs could be related to different treatment types, suggesting the need of implementing traditional tertiary treatment stages.

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