OCCURRENCE OF PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOATE (PFOA) IN N.E. SPANISH SURFACE WATERS AND THEIR REMOVAL IN A DRINKING WATER TREATMENT PLANT THAT COMBINES CONVENTIONAL AND ADVANCED TREATMENTS IN PARALLEL LINES.

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ABSTRACT

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are two emerging contaminants that have been detected in all environmental compartments. However, while most of the studies in the literature deal with their presence or removal in wastewater treatment, few of them are devoted to their detection in treated drinking water and fate during drinking water treatment. In this study, analyses of PFOS and PFOA have been carried out in river water samples and in the different stages of a drinking water treatment plant (DWTP) which has recently improved its conventional treatment process by adding ultrafiltration and reverse osmosis in a parallel treatment line. Conventional and advanced treatments have been studied in several pilot plants and in the DWTP, which offers the opportunity to compare both treatments operating simultaneously. From the results obtained, neither preoxidation, sand filtration, nor ozonation, removed both perfluorinated compounds. As advanced treatments, reverse osmosis has proved more effective than reverse electrodialysis to remove PFOA and PFOS in the different configurations of pilot plants assayed. Granular activated carbon with an average elimination efficiency of $64\pm11\%$ and $45\pm19\%$ for PFOS and PFOA, respectively and especially reverse osmosis, which was able to remove $\geq99\%$ of both compounds, were the sole effective treatment steps. Trace levels of PFOS (3.0-21 ng/L) and PFOA (<4.2-5.5 ng/L) detected in treated drinking water were significantly lowered in comparison to those measured in precedent years. These concentrations represent overall removal efficiencies of $89\pm22\%$ for PFOA and $86\pm7\%$ for PFOS.

1. Introduction

Perfluoroalkyl acids (PFAAs) are a subgroup of polyfluoroalkyl substances (PFASs) widely used in industrial and commercial applications for the past sixty years as water and oil repellents, fire retardants, herbicide and insecticide formulations, cosmetics, greases and lubricants, paints, polishes and adhesives. Although the literature discusses different families of PFAAs, perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are among the most commonly used, found in the environment and included in the international regulations (Giesy and Kannan, 2002; Kissa, 2001; Lindstrom et al., 2011). PFOA and PFOS are in the OSPAR List of Chemicals for Priority Action and recently, PFOS has been included as a persistent organic pollutant (POP) under the Stockholm Convention on Persistent Organic Pollutants (POPs) for global regulation of production and use (UNEP, 2010). A number of recent studies have indicated serious health effects associated with PFOS and PFOA in various animal models (Lau et al., 2007; Martin et al., 2010) and Post et al. (2012), reviews the more recent literature on health effects of PFOA. USEPA Science Advisory Board (US EPA, 2006) recommended PFOA be considered a likely human carcinogen although there is some uncertainty about the human relevance of some of the animal tumor data. Results of cancer incidence studies in communities with contaminated drinking water are forthcoming (Post et al., 2012). PFOA and PFOS are listed as chemical contaminants on the Drinking Water Contaminant Candidate List CCL3 considered for future regulation (US EPA, 2009a). Recently, PFOS has been included in the Proposal for a directive of the European Parliament and of the Council amending Directives 2000/60/EC and 2008/105/EC in regards to priority substances in the field of water policy (European Commission Proposal, 2012). In this Directive the environmental quality for the PFOS has been set (0.65 and 0.13 ng/L for the annual average of inland and other surface waters, respectively).

Sources of PFAAs in the environment come from the production of perfluorinated chemicals, fluorinated polymers, processing industry or from the use or disposal of consumer

products such as textiles treated with PFAAs, fire-fighting foams, household chemicals, carpets, degradation products or sewage sludge disposal, among others (Lindstrom et al, 2011; Post et al, 2012). The strong C-F bond renders PFAAs resistant to physical and metabolic degradation and makes them environmentally persistent (Kissa, 2001). Contrary to other typical POPs, the ionic nature, high solubility and negligible vapor pressure when dissolved in water of PFOA and PFOS make them highly mobile in an aqueous system, and therefore these compounds can be transferred from domestic, commercial, or industrial discharge to natural waters (Sinclair and Kannan, 2006). So far, they have been detected in rain and urban stormwater runoff (Eschauzier et al., 2010; Kwok et al., 2010; Xiao et al., 2012b), coastal and seawater (Ahrens et al., 2010; Alzaga and Bayona, 2004; Moller et al., 2010; Sánchez-Avila et al., 2010; Yamashita et al., 2004, 2005), wastewater (Alzaga and Bayona, 2004; Xiao et al.; 2012a; Yu et al., 2009a), surface water (Eschauzier et al., 2010; Hansen et al., 2002; Loos et al., 2008, 2009; McLachlan et al., 2007; Moller et al., 2010; Pistocchi and Loos, 2009), groundwater (Moody et al., 2003; Plumlee et al., 2008; Schultz et al., 2004) and tap water (Ericson et al., 2008, 2009; Eschauzier et al., 2012a; Haug et al., 2010; Lien et al., 2006; Mak et al., 2009; Post et al., 2009; Shivakoti et al., 2010; Skutlarek et al., 2006; Takagi et al., 2008, 2011; Ullah et al., 2011; Wilhem et al., 2010) throughout the world. Excellent reviews on the occurrence of polyfluorinated chemicals in the aquatic environment have recently been reported (Eschauzier et al., 2012b; Rumsby et al., 2009).

In Spain, the presence of PFAAs in the aquatic environment was first described in 2004 (Alzaga and Bayona, 2004). Table 1 summarizes the concentration ranges or the mean levels reported in the literature for the 2004-2012 period. Concentrations of relevant perfluorinated compounds in Spanish coastal waters, -up to 2.25 ng/L for PFOA and 8.38 ng/L for PFOS (excluding the Barcelona harbor) are substantially lower than those measured in some other parts of the world such as several Asian coasts (So et al., 2004; Yamashita et al., 2005) with maximum values of 68.6 ng/L for PFOA in Western Korea (Naile et al., 2010) which showed similar PFAAs pattern (PFOS concentration > PFOA concentration). In contrast, Spanish levels are higher than the

median values (around 1-2 ng/L for PFOA and <1 ng/L for PFOS) reported in S.E. Brazil (Quinete et al., 2009) and in the North Sea (0.07 ng/L) (Ahrens et al., 2010).

In Spain, the determination of PFAAs in wastewaters is restricted to a few effluents all located in the N.E. part of the country (Alzaga and Bayona, 2004; Sánchez-Avila et al., 2010; Gómez et al., 2011). Excluding the high values (100-300 ng/L) measured in one of the effluents (Alzaga and Bayona, 2004), the rest of Spanish wastewaters effluents ranged from 0.16 to 61.9 ng/L for PFOA and from <0.03 to 72.1 ng/L for PFOS. Both compounds are found in the same or even lower range than other industrialized countries such as Denmark (<2.0-24 ng/L for PFOA and <1.5-18 ng/L for PFOS) (Bossi et al., 2008); USA (2.5-97 ng/L for PFOA and 1.1-130 ng/L for PFOS) (Schultz et al., 2006); Japan (10-68 ng/L for PFOA and 42-635 ng/L for PFOS) (Murakami et al., 2009) or Korea for mixed wastewater from several wastewater treatment plants (WWTPs) (1100±1500 ng/L for PFOA and 110±220 ng/L for PFOS) (Kim et al., 2012). Moreover, the presence of PFAAs in sewage sludge from five WWTPs along the Llobregat River has been investigated (Llorca et al., 2011) with level ranges of 53.0-121.1 ng/g for PFOS and 7.0-30.3 ng/g for PFOA.

The occurrence of PFAAs in Spanish surface waters has been predominantly carried out in northeastern rivers. These Mediterranean rivers (Llobregat and Besós) are small streams with highly variable flows that lead to concentrations as high as 43 ng/L for PFOA and 275 ng/L for PFOS (Loos et al., 2009). The concentrations reported for other Spanish rivers are in the range of other worldwide rivers (Loos et al., 2009; Martin et al., 2010; McLachlan et al., 2007; Moller et al., 2010; Quinete et al., 2009; So et al., 2007). In European rivers, low levels of PFAAs in Nordic surface waters (i.e. <0.36 ng/L in Sweden) in comparison with the rest of Europe (i.e. Po, Rhine, and Seine Rivers) were present (Eschauzier et al., 2012b; McLachlan et al., 2007). Concentration levels measured in L'Albufera lake (Picó et al., 2012) for PFOA (up to 10.90 ng/L) and PFOS (up to 4.80 ng/L) are substantially lower than those found in lakes Erie and Ontario (Boulanger et al., 2004) and others cited herein.

Treated drinking water surveys of Spanish municipal waters were carried out in different metropolitan areas of the country (Ericson et al., 2008, 2009; Llorca et al., 2012a, 2012b). Maximum values of 57.43 ng/L (PFOA) (Ericson et al., 2009) and 258 ng/L (PFOS) were measured (Llorca et al., 2012a) but also significant concentration levels of other relevant compounds such as perfluorobutane sulfonate (PFBS) (up to 69.43 ng/L) or perfluorononanoate (PFNA) (up to 58.21 ng/L) were reported (see Table 1). These concentrations are fairly higher than all those found in the literature (Boiteux et al., 2012; Eschauzier et al., 2012b; Gellrich et al., 2013; Haug et al., 2010; Loos et al., 2007; Mak et al., 2009; Martin et al., 2010; Post et al., 2009; Rumsby et al., 2009; Thompson et al., 2011).

The presence of PFAAs in surface and tap waters indicates the incomplete removal in sewage treatment plants, industrial discharges (e.g. from facilities making or using PFAAs) and potabilization processes. Levels of PFOS and PFOA were higher in effluents from wastewater facilities than those measured in influents (Loganathan et al., 2007; Sinclair and Kannan, 2006; Yu et al., 2009a) and there is some conflicting evidence about the ability of drinking water treatment processes to remove PFAAs (Rumsby et al., 2009). Thus, granular activated carbon (GAC) proved to be effective for the elimination of PFOS and PFOA homologues at batch scale (Ochoa-Herrera and Sierra-Alvarez, 2008; Yu et al., 2009b) and in potabilization processes but not for the more hydrophilic shorter chain PFAA (i.e. perfluorobutanoate and PFBS) (Eschauzier et al., 2012b; Wilhem et al., 2010). However, other reports indicated a moderate removal (Quiñones and Snyder, 2009; Shivakoti et al., 2010) or limited in time (Takagi et al., 2011). The use of reverse osmosis (RO) and nanofiltration (NF) as advanced drinking water treatments is still limited but both technologies have been shown to be successful for the removal of >C5 PFAAs (Loi-Brugger et al., 2008; Tang et al., 2006).

In view of the PFASs levels in different aquatic compartments measured in our country, the aim of this work was to study the occurrence of the two most well-characterized PFAAs, PFOA and PFOS in the Llobregat River (N.E. Spain), which supplies raw surface water to the Barcelona's

drinking water treatment facility, and their removal during the potabilization process. This plant, which combines conventional and recently updated advanced treatments, potentially leads to a better understanding of those water treatment steps which can efficiently remove PFAAs.

2. Materials and methods

2.1. Standards and reagents

All reagents used were of analytical or high-performance liquid chromatographic grade. Analytical standards of perfluoro-n-octanoic acid (PFOA) and potassium salt of perfluoro-1-octanesulfonate (PFOS) were purchased from Aldrich (Steinheim, Germany). The internal standards $^{13}C_4$-sodium perfluoro-1-octanesulfonate (>99%) ($^{13}C_4$-PFOS), $^{13}C_4$-perfluoro-n-octanoic acid (>99%) ($^{13}C_4$-PFOA) and $^{13}C_2$-perfluoro-n-decanoic acid (>99%) ($^{13}C_2$-PFDA) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Methanol, dichloromethane and hydrochloric acid (HCl) were provided from Merck (Darmstadt, Germany). Isopropyl alcohol was from Carlo Erba (Rodano, Milan, Italy), L(+)-ascorbic acid was from Panreac (Barcelona, Spain). High purity water produced with a Milli-Q Synergy UV system (Millipore, Bedford, MA, USA) was used.

All stock standard solutions (50 ng/µL) were individually prepared by weight in methanol and stored at 4 ºC. Intermediate solutions were prepared weekly from the stock standard solution by appropriate dilution in methanol. Calibration standard solutions ranging from 1 to 300 pg/µL of PFOA and 0.5 to 500 pg/µL of PFOS were prepared daily with 50 and 150 pg/µL of the labeled compounds, respectively.

Nitrogen (99.999% pure) and high-purity argon (Ar_1) supplied by Air Liquide (Madrid, Spain) was used for the electrospray ionization (ESI) source and as a collision-induced dissociation (CID) gas in the triple quadrupole, respectively.

2.2. Water collection

A total of 131 samples were collected between 2002 and 2012 including: 32 Llobregat River waters (2002-2007); 27 water samples of pilot plant studies using different advanced treatments (2005-2007); 46 water samples collected at different steps of the purification processes in the drinking water treatment plant (DWTP) under study (2008-2012); and finally 26 raw groundwater samples involved in the potabilization process (2009-2012). The DWTP selected for this study treats about 4 m^3/s of Llobregat surface river water and supplies over one million inhabitants. This Mediterranean river can exhibit highly variable water flows and therefore fluctuations in water quality are observed. The potabilization process has been modified several times in recent decades in order to improve the quality of the final treated drinking water. At present it consists of dioxychlorination, coagulation, flocculation, settling, sand filtration (SF) and raw groundwater dilution to improve raw surface water quality. At this stage, the water is splitted in two lines following a conventional treatment (~50%) and an advanced treatment (~50%). The former consists of ozonation (O_3) and GAC filtration whereas the latter consists of ultrafiltration (UF) followed by ultraviolet (UV) disinfection, RO and remineralization with calcite. Then, treated waters from both lines are blended, chlorinated and distributed. More details of the drinking water treatment processes and the scheme of the DWTP under study are enclosed in the Supporting information section (Text S1 and Fig. S1, respectively).

GAC (1250 tonnes) installed in the DWTP are distributed in 24 filters. The GAC types used are Chemviron F-400 (density 440 kg/m^3; 12 filters), Norit ROW 0.8 (density 381 kg/m^3; 2 filters) and Norit 1240 EN (density 485 kg/m^3; 6 filters). The remaining filters are used to regenerate exhausted carbon and some are empty spaces for the maintenance of civil works. GAC is regenerated before it reaches an iodine adsorption coefficient of 450 mg/L, whereas RO concentrates are discharged directly to the Mediterranean Sea.

River water samples, raw groundwater and water from the different stages were collected as grab samples. The latter were collected taking into account the hydraulic retention time (HRT) of each step to assess the efficiency of each one.

2.3. Sample extraction

Samples were collected in 1L Pyrex borosilicate amber glass bottles and were stored at 4 ℃ prior to extraction. In order to minimize the possibility of introducing PFOA and PFOS contamination into samples, fluoropolymer materials were avoided. Those samples containing residual chlorine were quenched with ascorbic acid. Water samples were concentrated using liquid-liquid extraction (LLE) according to the method developed by Barco et al. (2003) with slight modifications. Briefly, 200 or 1000 mL of superficial or treated drinking water, respectively, were used for extraction after adjusting pH to 2 using an HCl diluted solution. Internal standards, $^{13}C_4$-PFOA and $^{13}C_4$-PFOS were added for the quantification by the isotope dilution method. Then, water samples were extracted with 2 x 100 mL of dichloromethane/isopropyl alcohol (90:10 v/v). Extracts were filtered through a Whatman paper filter (Maidstone, U.K.). The two collected extracts were put together and evaporated to dryness at 40 ℃ under a gentle nitrogen flow. The extract was reconstituted with 500 µL of methanol including $^{13}C_2$-PFDA added as performance standard and finally filtered through 0.22 µm nylon syringe filter.

2.4. Instrumental analysis

A TSQ Quantum triple quadrupole mass spectrometer equipped with ESI source (Thermo Fisher Scientific, San Jose, CA, USA), a Finnigan Surveyor MS plus pump and a HTC PAL autosampler were used for the analysis by liquid chromatography tandem mass spectrometry (LC-MS/MS). The quadrupoles of mass spectrometer are hyperbolic and allows to work at high-

resolution selected reaction monitoring (H-SRM)/high resolution and to perform accurate mass (AM) measurements with errors lower than 5 mDa.

The chromatographic separation was performed on a reversed-phase C_{18} Hypersil Gold column (50 x 2.1 mm, 1.9 μm, Thermo Fisher Scientific, San Jose, CA, USA) preceded by an C_{18} XBridge guard column (10 x 2.1 mm, 2.5 μm, Waters, Mildford, MA, USA). The mobile phase was composed of Milli Q water as solvent A and methanol as solvent B at a flow rate of 200 μL/min. The linear gradient elution program was: 30% methanol up to 100% methanol in 7 min. This percentage was then maintained for 3 min and return to initial conditions for 10 min.

The analyses were carried out in ESI negative ion mode with the spray voltage at 3.5 kV and the optimum tube lens voltage (TL) for each m/z. The ion transfer tube temperature was set at 350 ºC. Nitrogen (purity 99.999%) was used as a sheath gas, ion sweep gas and auxiliary gas at flow rates of 30 psi, 0 and 5 a.u. (arbitrary units), respectively. Data were acquired in MS/MS with H-SRM. In H-SRM mode a peak width of 0.1 and 0.7 Da Full width at half maximum (FWHM) on Q1 and Q3, respectively, and a scan width of 0.01 Da were used. The argon CID gas was used at a pressure of 1.5 mtorr and the optimum collision energy (CE) for each transition was selected. For quantitative purposes, two transitions for each compound were monitored, one for quantification and the second for confirmation and ratio between transitions was calculated (European Commission, 2002). The optimum MS/MS conditions are displayed in Table S1 of the Supporting information section. Data acquisition was performed with Xcalibur 2.0.7 software (Thermo Fisher Scientific).

To optimize the source, transmission and MS/MS conditions, a 1 ng/μL stock solution in methanol of each compound was infused at a flow rate of 5 μL/min by the syringe pump integrated into the TSQ instrument and mixed with the mobile phase (200 μL/min, methanol:Milli Q water (50:50, v/v)) using a Valco zero dead volume tee piece (Supelco,USA).

2.5. Quantification, quality control and quality assurance

Quantification of analytes was performed using the isotope dilution method. Since 2005, labeled $^{13}C_4$-PFOA and $^{13}C_4$-PFOS were used as internal standards and previously, external calibration was applied. At an early stage of the method validation a series of experiments to determine the precision and accuracy of the extraction and analytical procedures were carried out. To determine the recovery of PFOA and PFOS, a PFOA/PFOS mix was spiked at two concentration levels (10 and 150 ng/L for PFOA and at 5.0 and 250 ng/L for PFOS) into pristine bottled water and then, these samples were extracted following the same procedure used for real samples. The calculated recoveries were 86-95% and 69-82% for PFOA and PFOS, respectively. To check the recoveries in all samples, the recovery of internal standards ($^{13}C_4$-PFOA and $^{13}C_4$-PFOS), added before extraction, were calculated relative to $^{13}C_2$-PFDA, added after extraction. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as the mean of the signal of a blank sample (pristine bottled water, n=5) plus three and tenfold the standard deviation, respectively. The LOD was determined to be 1.9 and 0.4 ng/L for PFOA and PFOS, respectively and the LOQ was determined to be 4.2 and 1.1 ng/L, respectively. To minimize background contamination throughout the procedure, all known sources of contamination, including accessible polytetrafluoroethylene (PTFE) and other fluoropolymer materials from the instruments and apparatus, were removed. Blank field samples and blank spikes were used as quality controls.

A blank sample was always extracted with every batch of samples showing good repeatability for the method. Instrumental blanks (methanol) were injected between samples and three additional blanks were injected after the most concentrated internal calibration standard in order to avoid cross talking between injections. External quality assurance was performed by participation in two inter-laboratory trials: one for PFOS and PFOA measurements in water samples (Yamashita et al., 2007) and the other for study on perfluorinated chemicals (van Leeuwen et al., 2009).

For identification purposes the following criteria were accomplished: i) the ratio of the

chromatographic retention time of the analyte to that of the internal standard, shall correspond to that of the calibration solution at a tolerance of ±2.5%; ii) two m/z transitions were confirmed for each analyte; iii) the ratio between the two transitions in the sample compared to ratio in the calibration curve should be in agreement to [calibration curve average ± maximum permitted tolerances for relative ion intensities as proposed in European Commission (2002)], corresponding to 3.9±25% and 1.8±20% for PFOA and PFOS, respectively.

2.6. Matrix effects

Matrix components present in the sample extracts have potential to cause ionization suppression or enhancement of electrospray signal. In order to routine control we checked that the areas of labeled internal standards injected in the same day remained approximately constant (tolerance ±15%) ensuring these matrix effects were controlled. The concentration of labeled internal standards added in all samples and calibration standard solutions is constant (50 and 150 pg/µL in final extract), if matrix effects exist, the response of extraction standards taking into account the recovery of each sample, and the response of performance standards should look affected and will not be constant.

3. Results and discussion

In an early stage of this work (2002-2005), a study on the presence of PFOA and PFOS along the course of the Llobregat River was performed to determine the levels of these compounds in the river. Due to their presence in some of the surface waters it was decided to control their level in the Llobregat River raw surface water entering the DWTP (years 2005-2007). In parallel, a series of experiments in pilot plants were performed in order to improve the quality of the final treated

drinking water. Four different scenarios mainly focused on combinations of advanced treatments such as UF, RO and reverse electrodialysis (RED) were considered to monitor the behavior of PFOA and PFOS in these pilot plants.

Next, the removal of PFOA and PFOS in each individual stage of the DWTP was studied. During the period from 2008-2009 the DWTP was operating using a conventional treatment and since 2010 a new potabilization process of the DWTP was set up by adding a supplementary line (UF, UV disinfection, RO and remineralization).

3.1. PFOA and PFOS in Llobregat River samples

Superficial water samples collected along the course of the Llobregat River (n=30) had already been analyzed in 2002-2005. At that time, the concentration levels ranged from <4.2 to 130 ng/L for PFOA and <1.1 to 11120 ng/L for PFOS respectively, although only 10% and 30% of the analyzed samples exhibited levels above the LOQ. Samples from the confluence with its tributary river Anoia and Abrera exhibited high levels of PFOS (860-11120 ng/L) attributed to two industrial point sources in the river. The remaining levels (<1.1-430 ng/L of PFOS, mean 54 ng/L) are in the same order than those measured in major European rivers (Eschauzier et al., 2012b; Loos et al., 2009; McLachlan et al., 2007; Moller et al., 2010), thus confirming the occurrence of these ubiquitous compounds.

PFOA and PFOS in the Llobregat River raw surface water entering the DWTP have been measured since 2005. Determinations carried out during the period 2005-2007 (n=10) exhibited concentration ranges of <4.2 to 1470 ng/L for PFOA and <1.1 to 10980 ng/L for PFOS, attributed to the important industrial activity in this area of the Llobregat River. Six out of ten samples exhibited concentrations of PFOS >610 ng/L and only one sample had a concentration below the LOQ. However, the maximum concentration (10980 ng/L) was still three fold lower than the proposed maximum allowable concentration for PFOS and its derivative salts in inland surface waters (36000

ng/L), established recently by the European Commission (European Commission Proposal, 2012). On the other hand, 50% of the samples have PFOA levels below the LOQ and only one sample show a high concentration (1470 ng/L).

Since then, the concentrations of PFOS and PFOA in the Llobregat River raw surface water entering the DWTP have been gradually declining probably as a result of reductions in emissions and production volumes due to implemented regulations in 2006 (European Commission, 2006) relating to restrictions on the marketing and use of certain dangerous substances and preparations (PFOS). As shown in more detail in Table 3, the concentrations ranged from 4.9 to 44 ng/L for PFOA (mean 15 ± 13 ng/L) and from 20 to 348 ng/L for PFOS (mean 104 ± 94 ng/L) during the latter period (2008-2012, n=10).

3.2. Behavior of PFOA and PFOS in a DWTP

As already mentioned, since 2005, different configurations of pilot plants involving combinations of UF, RO and RED were tested. Four scenarios were studied: $UF+RED+O_3+GAC+Cl_2$; $SF+RED+O_3+GAC+Cl_2$; $UF+50\%[RO]+50\%[O_3+GAC+Cl_2]$; and $UF+50\%[RED]+50\%[O_3+GAC+Cl_2]$. These experiments were performed in order to study the efficiency of these processes to remove PFOA and PFOS among other emerging compounds (Agbar, unpublished results) once proved the presence of PFAAs entering the DWTP. From these different scenarios, RED was able to remove PFOA in a range from 57 to 100% and 26 to 100% for PFOS depending on the configuration used. When RO was assayed, removals were always higher than 99%. Thus, the high efficiency of RO in drinking water treatment processes to eliminate PFOA and PFOS at low concentrations (ppt-range) was proved. These results were in agreement with the feasibility of RO membranes for treating wastewaters containing PFOS with removals of 99% or even higher, with feed concentrations at the ppm level (Tang et al., 2006, 2007).

At that time, the conventional potabilization process consisting of

chlorination/dioxychlorination, coagulation, flocculation, settling, sand filtration, raw groundwater dilution, ozonation, GAC filtration and a final postchlorination step was still in operation. The new advanced treatment process was set up in 2010 after choosing the most effective configuration of the different tested pilot plant scenarios, which provided the best results for a wide range of emerging pollutants.

Thus, the final design of the DWTP, consisting in adding a parallel treatment line after sand filtration and raw groundwater dilution and before ozonation. It included UF followed by UV disinfection, RO and remineralization. This line accounts around 50% of treated water, which is then blended with the GAC filtered water (~50%) coming from the conventional treatment. Blended water from the two line treatment processes is postchlorinated before leaving the plant. This configuration allowed us to study simultaneously the behavior of target compounds in two different potabilization treatments: conventional and advanced.

3.2.1. PFOA and PFOS behavior during conventional water treatment

Table 3 summarizes the concentration ranges of PFOA and PFOS and the removals measured in the different treatment steps of the DWTP. Results (n=10) from the conventional treatment refer to years 2008-2012. Fig. 1 displays the concentrations of PFOA and PFOS in relevant stages of the treatment process in the four and two campaigns sampled in 2008 and 2009, respectively. Overall levels of analytes were higher in autumn-winter than in spring-summer with significant differences of concentrations at the intake of the DWTP. This behavior observed for both compounds were more significant in the PFOS for which concentrations were higher, around 100 ng/L in autumn-winter and 25 ng/L in spring-summer.

In all cases concentrations from both PFAAs did not vary considerably in raw surface water, prechlorinated/dioxychlorinated and sand filtered stages (see removals in Table 2) which is in agreement with the behavior observed in several DWTPs (Eschauzier et al., 2010, 2012a, 2012b; Rumsby et al., 2009; Shivakoti et al., 2010; Takagi et al., 2011). The following step consists of

blending sand filtered water with raw groundwater at varying percentages (~0-30%) to improve water quality. Concentration ranges of 31-32 ng/L for PFOA and 49-72 ng/L for PFOS were measured in 2009 for raw groundwater samples. This raw groundwater contamination can be at least partially associated with treated water infiltration practices to recharge the aquifer and proves that this blending can be an additional source of pollution in the DWTP. Ozonation is the following step of the potabilization process and the results showed that it does not affect the concentrations of PFAAs (see removals in Table 2). The ineffectiveness of ozone to degrade PFAAs is in agreement with batch experiments (Schröder and Meesters, 2005) and those observed in other water purification plant processes (Shivakoti et al., 2010; Thompson et al, 2011) and can be explained by the strength of the C-F bond in PFAAs. In addition, the ozonation of PFOS/PFOA precursors may result in an increase in the concentrations of PFOS and PFOA. The increase has been observed in wastewater treatment during which bacteria can convert the precursors to PFOS/PFOA (Xiao et al., 2012a). Taking into account that the concentration of ozone used in the DWTP under study was around 5 mg/L and the contact time 20 minutes, the low concentrations of precursors appear to be the reason of the absence of increase of PFOA and PFOS concentrations. Once ozonated, water is GAC filtered. GAC filters removed about 45±19% of PFOA and 64±11% of PFOS in all samples analyzed (Table 2). Critical factors for an efficient removal of pollutants are the water matrix, the type of carbon, the GAC usage rate and the GAC loading. The latter has been reported to be a key factor for an efficient removal of both compounds in Japanese DWTPs performing better when used for less than one year (Takagi et al., 2011). Eschauzier et al. (2012a) found removals of 50% for PFOA and full elimination of PFOS after the GAC filtration and also observed the enrichment of branched PFOA and PFOS isomers relative to non branched isomers during GAC filtration. In 2011, a maximum of 65 hm^3 of water was purified in the DWTP. This corresponds to a maximal total loading of 52 m^3 H$_2$O/kg GAC to prevent breakthrough of analytes. In our case, the measured concentrations after GAC filtration are the average result of the 24 GAC filters installed in the DWTP, which are regenerated sequentially approximately once a year due to the very poor raw

surface water quality. In this context, depending on the number of regenerated filters when the samples were taken, the removal can vary considerably. Their results agree in general with the previous results regarding the removal mechanisms of PFOS and PFOA by coagulation and enhanced coagulation during drinking water treatment (Xiao et. al, 2013). The results obtained in this article suggest that primary PFOS/PFOA removal mechanism is adsorption to coagulant.

Mean values of PFOA and PFOS for treated drinking water in the conventional treatment (2008-2009) were 13±11 ng/L and 33±24 ng/L, respectively, which represent overall removal efficiencies of 52%±31 for PFOA and 69%±12 for PFOS (Table 2). These levels are among the higher concentrations reported in several countries (Mak et al., 2009), far away from 1.45 ng/L and 0.20 ng/L for PFOA and PFOS measured in Norway (Haug et al., 2010), but very close to tap water levels reported in Catalonia (N.E. Spain) (Ericson et al., 2009) (see Table 1).

3.2.2. PFOA and PFOS behavior in advanced water treatment

As the new advanced treatment process added a parallel treatment line that included UF and RO, this DWTP offers an interesting opportunity to compare a conventional treatment with GAC filtration as the effective treatment step with an advanced treatment train.

During the 2010-2012 period when the advanced treatment was already in operation, the removal of both compounds in the conventional treatment line followed the same behavior as described before with insignificant variations after prechlorination/dioxychlorination, sand filtration and ozonation (see removals in Table 2). For raw groundwater samples which are blended with sand filtered water, concentration levels were of the same order as those reported in previous years. Thus, ranges of 15-26 ng/L for PFOA and 61-86 ng/L for PFOS, respectively were measured and representing a source of PFAAs in the pretreated water. Eliminations of 41% for PFOA and ~63% for PFOS from raw surface water to GAC filtered water (see Fig. 2 and Table 2) were observed. Concentration ranges of GAC filtered water were <4.2-7.4 ng/L (mean 4.7±2.2 ng/L) for PFOA and 8.6-35 ng/L (mean 22±13 ng/L) for PFOS, respectively. In parallel, in the advanced treatment line

(2010-2012 period), the elimination of both PFAAs was irrelevant after ultrafiltration but complete (≥99%) after RO membranes passage as shown in Table 3. The RO outlet concentrations of PFOA were < 4.2 ng/L whereas for PFOS ranged from <1.1 to 1.3 ng/L. In agreement with this behavior, the efficiency of RO for the complete removal of PFOA, PFOS and other perfluoroalkyl acids at water reclamation plants in Australia was demonstrated (Thompson et al., 2011). Fig. 2 displays the behavior of the two compounds at the different stages of the conventional and advanced treatment in the four campaigns studied.

The final treated drinking water is obtained by postchlorination of the blended GAC filtered waters from conventional treatment and remineralized water from the advanced process. However, the advanced treatment when blending the two water lines provides treated drinking water that is not completely free from perfluorinated compounds, specifically for PFOS, due to the input of GAC line. This leads to concentration ranges of <4.2-5.5 ng/L for PFOA and 3.0-21 ng/L for PFOS in final treated drinking water which are substantially lower than those measured with the former potabilization process. These levels represent an overall removal percentage of 89±22 for PFOA and 86±7 for PFOS, respectively, as shown in Table 2.

Drinking water has been identified as one of the major routes of human exposure (Skutlarek et al., 2006). Post et al. (2012) provide an excellent critical review of recent literature on PFOA as an emerging drinking water contaminant. This review demonstrates that relatively low levels of PFOA in drinking water can substantially increase total human exposure. For example, ongoing exposure to 40 ng/L would lead to a serum levels over the general population mean of 4 ng/ml. Thus, on average, 100:1 ratio exists between serum level increase and drinking water concentration. Accordingly, internationally several authoritative bodies have issued drinking water guidance for PFOS and PFOA, based on human health effects on a different precautionary action value ranging from 40 to 9000 ng/L (DWI, 2007; NJDEP, 2007, 2009; Renner et al., 2007; Rumsby et al., 2009; US EPA, 2009b; Wilhelm et al., 2008). There are not any drinking water recommended levels for PFAAs in Spain. Therefore, taking as a reference the more restrictive individual guidance levels, i.e.

40 ng/L (preliminary health-based guideline value, New Jersey) and 200 ng/L (Provisional Health Advisory, US EPA) for PFOA and PFOS, respectively, all treated drinking samples exhibited significant lower levels of the two pollutants both in the advanced and conventional treatments. Additionally, taking into account the levels of PFOA found in treated drinking water after conventional and advanced treatments (13 ng/L and 3 ng/L, respectively), the calculated chronic daily intake (CDI) for an adult of 70 Kg body weight assuming an intake of 2 L water/day every day would be 0.37 ng/kg/day and 0.09 ng/Kg/day, respectively. For PFOS, the CDI would be 0.94 ng/Kg/day and 0.37 ng/Kg/day coming from concentrations of 33 ng/L (conventional treatment) and 13 ng/L (advanced treatment) treated drinking waters. The provisional oral reference dose (RfD) for PFOA and PFOS has been established in 333 ng/Kg/day and 25 ng/Kg/day (Gulkowska et al., 2006) and the tolerable daily intake (TDIs) recently recommended by the European Food Safety Authority (EFSA, 2008) for PFOA and PFOS were 1500 ng/Kg/day and 150 ng/Kg/day. Therefore, both CDIs would be considerable lower than the provisional RfD values and recommended TDIs for PFOA and PFOS.

4. Conclusions

The presence of PFOA and PFOS in surface water samples and at the different stages of a drinking water treatment plant has been proved. PFOS was predominant over PFOA in all samples (surface, raw groundwater and different treatment steps of the DWTP including treated drinking water). Conventional and advanced treatment efficiency to remove both compounds was studied and compared in several pilot plants and in a DWTP that operate with both treatments in parallel lines. In the different configurations of pilot plants assayed RO has proved more effective than RED to remove PFOA and PFOS for advanced treatments. On the other hand, in the DWTP study, some of the potabilization steps such as preoxidation, sedimentation, sand filtration or ozonation have an irrelevant impact on the removal of both compounds. However, GAC filters used in the

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conventional treatment line and RO in the advanced treatment line were able to remove significantly PFOA and PFOS to low concentrations (ppt-range), particularly the latter. Overall, removal efficiencies have been about 89±22% of PFOA and 86±7% of PFOS. Raw groundwater represents a constant source of PFAAs in the pretreated water when blended with sand filtered water. The results obtained showed that conventional treatments do not completely provide treated drinking water free from perfluorinated compounds, and therefore minimize their levels in raw surface water by avoiding discharges or improving wastewater treatments is essential. Nonetheless, maximum values found within the final treatment, through the combining of conventional and advanced technology, were an order of magnitude lower than most precautionary guidance published and both CDIs, taking into account the levels of analytes found in treated drinking water after conventional and advanced processes, would be considerable lower than the provisional RfD values and recommended TDIs for PFOA and PFOS. Therefore, it is not expected to pose human health risks.

Acknowledgements

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Figure captions

Fig. 1: Concentration levels of PFOS and PFOA (ng/L) in 2008-2009 through the conventional treatment potabilization process of the DWTP.

Fig. 2: Concentration levels of PFOS and PFOA (ng/L) in 2010-2012 through the conventional and advanced potabilization process of the DWTP.

Treated: Blending of ~50% (conventional treatment) and ~50% (advanced treatment).
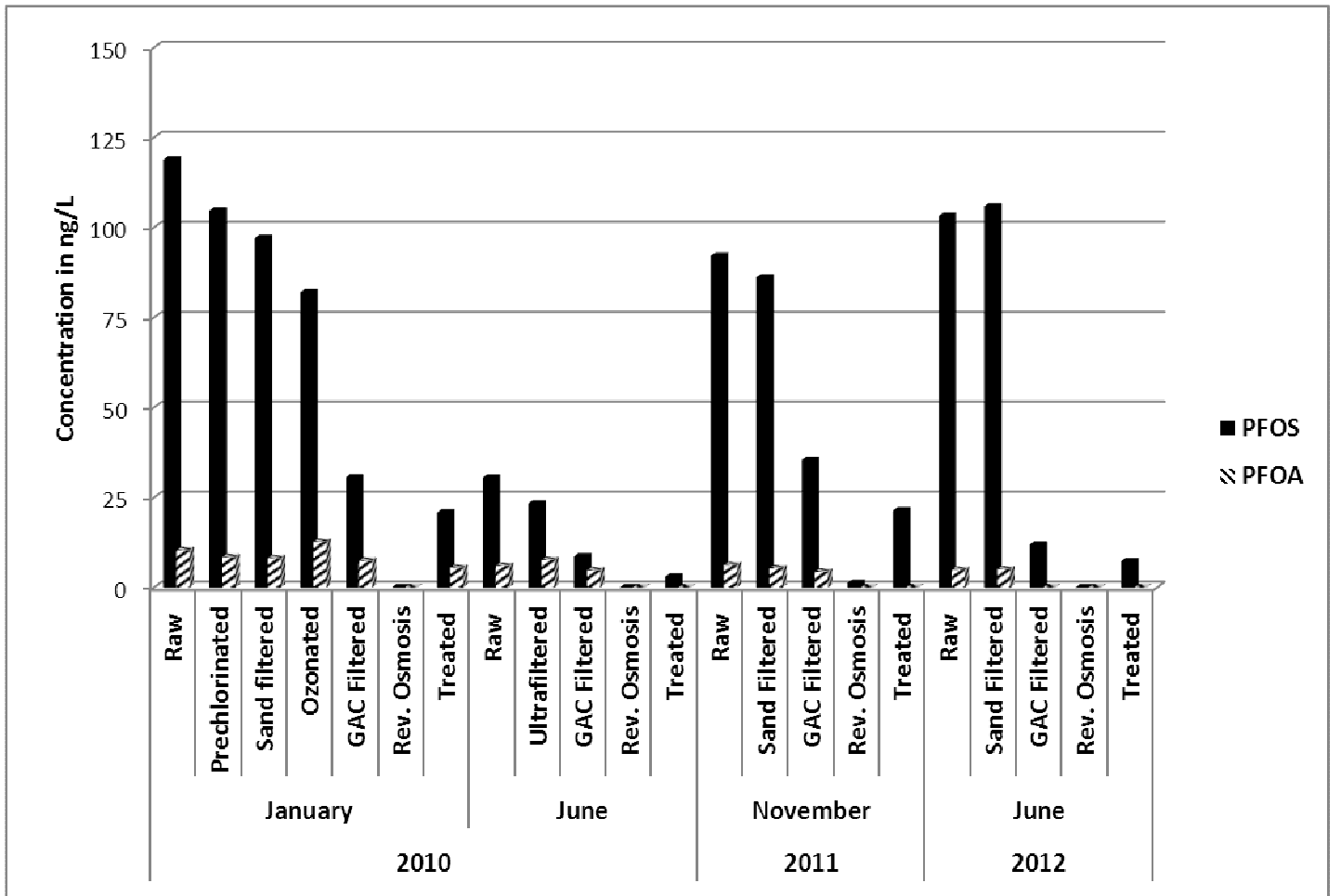
HIGHLIGHTS

PFOA/PFOS behavior was studied in a DWTP with conventional and advanced treatments.

PFOA and PFOS were not fully eliminated during conventional drinking water treatment.

Reverse osmosis effectively removes PFOA and PFOS in the potabilization process.

GAC filters used in the conventional treatment removed significantly PFOA and PFOS.
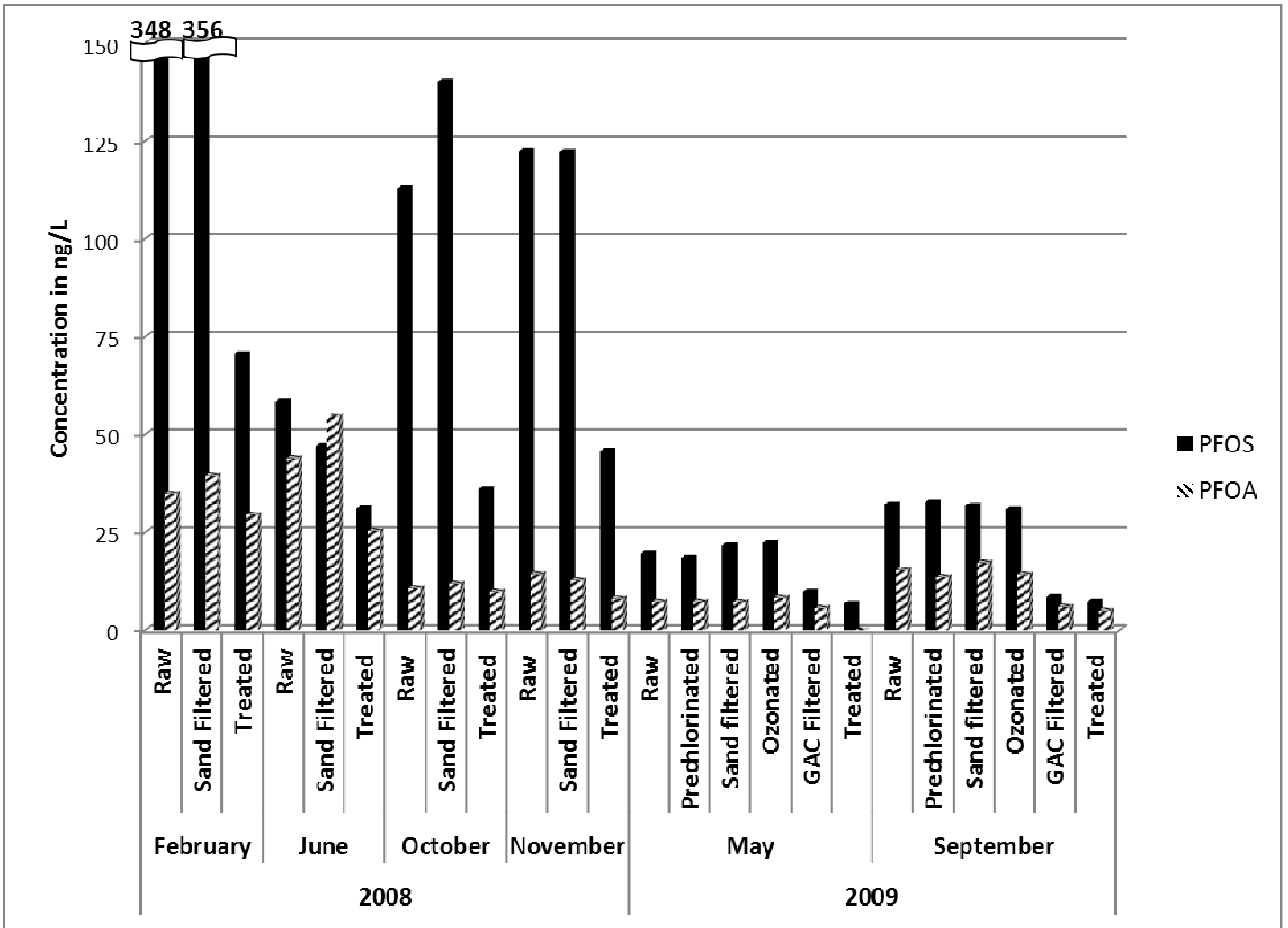
Table 1. Perfluorinated compounds in Spanish water samples (2004-2012). Mean or concentration ranges expressed in ng/L.

	PFBS	PFHxS	PFHxA	PFHpA	PFOS	PFOA	PFNA	PFDA	PFUnDA	References
Coastal waters										
Barcelona harbor						<100-340		<20-650		Alzaga and Bayona (2004)
Catalan coastal	<0.07-0.24	<0.03-0.47			<0.03-3.93	<0.08-1.86	<0.06-1.35			Sánchez-Avila et al. (2010)
Catalan harbors	<0.07-0.23	<0.03-2.09			<0.03-8.38	0.38-2.25	<0.06-1.35			Sánchez-Avila et al. (2010)
Cantabric harbors	nd-1.25	nd-0.19			0.01-6.57	0.05-0.31	0.04-0.20			Gomez et al. (2011)
Wastewaters (effluents)										
WWTP (N.E. Spain)						100-4300		50-8170		Alzaga and Bayona (2004)
WWTP (N.E. Spain)						<100		<100		Alzaga and Bayona (2004)
WWTP (N.E. Spain)	<0.07-2.03	<0.03-25.80			<0.03-72.10	3.47-61.90	<0.06-0.84			Sánchez-Avila et al. (2010)
WWTP (N.Spain)	nd-5.08	0.05-0.31			0.09-5.11	0.16-3.53	0.04-1.40			Gómez et al. (2011)
Surface waters (rivers and lakes)										
Guadalquivir River			6.20	1.58		4.60	1.02			McLachlan et al. (2007)
Francolí River	<0.27	0.78	<0.87	3.38	5.88	24.90	0.64	<0.82	<0.43	Ericson et al. (2008)
Ebro River	<0.27	<0.43	<0.87, nd	0.72, 1	1.59	1.90, 2	<0.44, nd	<0.82, 1	<0.43, 1	Ericson et al. 2008; Loos et al. (2009)
Llobregat River			17	nd	254	43	15	1	1	Loos et al. (2009)
Besós River			11	8	275	41	13	6	1	Loos et al. (2009)
Sar River			nd	nd	6	6	nd	1	nd	Loos et al. (2009)
Catalan Rivers	<0.07-0.88	<0.03-0.64			1.09-9.56	0.79-9.63	<0.06-1.62			Sánchez-Avila et al. (2010)
L'Albufera lake	nd-<0.02		<0.02-0.10	<0.02-0.95	0.10-4.80	0.03-10.90	nd-1.24	nd-1.25		Picó et al. (2012)
Drinking water										
Tarragona area	<0.27	<0.18-0.28	<0.87	<0.61-3.02	0.39-0.87	0.32-6.28	<0.42-0.52	<0.82	<0.43	Ericson et al. (2008)
Catalonia	<0.07-69.43	<0.02-5.30	<0.17-8.55	<0.47-18.40	<0.12-58.12	<0.85-57.43	<0.15-58.21	<0.12-10.00	<0.07-4.23	Ericson et al. (2009)
Barcelona area	<0.02-36	<0.02-4.4	<0.07-10	<0.05-16	<0.005-258	<0.1-35	<0.01-22	<0.04-4.7	<0.28-3.8	Llorca et al. (2012a,b)
Ebro River basin	<0.02-0.43	<0.02-0.56	<0.07-2.9	<0.05-<0.2	<0.005-1.3	<0.1-0.49	<0.01-0.48	<0.04-3.0	<0.28-2.7	Llorca et al. (2012a,b)
Valencia area	<0.02-2.1	<0.02-28	<0.07-1.7	<0.05-0.55	<0.017-27	<0.1-7.6	<0.01-0.70	<0.04-0.72	<0.28-0.72	Llorca et al. (2012a,b)
Guadalquivir River basin	<0.02-<0.1	<0.1	<0.2	<0.2	<0.017-1.5	<0.1-2.1	<0.03-1.2	<0.13	<0.9	Llorca et al. (2012a,b)

nd = not detected. Acronyms: PFBS:Perfluorobutane sulfonate; PFHxS: Perfluorohexane sulfonate; PFHxA: Perfluorohexanoate; PFHpA: Perfluoroheptanoate; PFOS:

Perfluorooctane sulfonate; PFOA: Perfluorooctanoate; PFNA: Perfluorononanoate; PFDA: Perfluorodecanoate; PFUnDA: Perfluoroundecanoate.

Table 2. Concentration ranges in ng/L and removals of PFOA and PFOS measured in each potabilization step of the DWTP under study.

Sample Reference	n	Conventional Treatment PFOA Ranges	PFOA Mean ±SD	PFOA % Removal	PFOS Ranges	PFOS Mean ±SD	PFOS % Removal	n	Conventional and Advanced Treatment PFOA Ranges	PFOA Mean ±SD	PFOA % Removal	PFOS Ranges	PFOS Mean ±SD	PFOS % Removal
Raw Surface	6	7.4-44	21±15	-	20-348	116±121	-	4	4.9-10	6.9±2.4	-	31-119	86±39	-
Prechlorinated/ Dioxychlorinated	2	7.3-14	10±4.5	11±15	19-33	26±10	3±4	1	8.4	-	nc	105	-	nc
Sand Filtered	6	7.3-55	24±19	2±4	22-356	120±126	3±8	3	5.1-8.1	6.2±1.7	6±8	97-106	96±9.9	5±4
Raw groundwater [a]	2	31-32	32±0.7	-	49-72	61±16	-	2	15-26	21±7.8	-	61-86	74±18	-
Ozonated	2	8.3-14	11±4.3	9±12	22-31	27±6.1	2±2	1	13	-	nc	82	-	nc
GAC Filtered	2	5.7-6.0	5.9±0.2	45±19	8.5-9.9	9.2±0.9	64±11	4	<4.2-7.4	4.7±2.2	41 [c]	8.6-35	22±13	63 [c]
Ultrafiltered	-	-	-	-	-	-	-	1	7.6	-	nc	23	-	nc
Reverse Osmosis	-	-	-	-	-	-	-	4	<4.2	2.1±0	100±0	<1.1-1.3	0.7±0.4	99±1
Treated Drinking [b]	6	<4.2-30	13±11	**52±31** [d]	6.9-71	33±24	**69±12** [d]	4	<4.2-5.5	3.0±1.7	**89±22** [d]	3.0-21	13±9.4	**86±7** [d]

Conventional treatment (years 2008-2009); advanced treatment (years 2010-2012).

[a] Raw groundwater (~0-30%) was blended with sand filtered water and diverted to conventional and advanced treatment lines.

[b] Treated water was a blending of ~50% (conventional treatment) and ~50% (advanced treatment).

[c] Only one data of removal.

[d] In bold: Overall removal.

<LOQ taken as LOQ/2 (2.1 ng/L for PFOA and 0.5 ng/L for PFOS) for statistical calculations (mean and standard deviation).

n: number of samples; SD: standard deviation; -: not applicable; nc: not calculated (n=1).

1   **Table 3.** Concentration ranges of PFOA and PFOS (in ng/L) measured in different potabilization

2   steps of a DWTP (mean, standard deviation, number of samples).

	Conventional treatment		Conventional and advanced treatment	
	PFOA	PFOS	PFOA	PFOS
Raw	7.4-44 (21, 15, 6)	20-348 (116, 121, 6)	4.9-10 (6.9, 2.4, 4)	31-119 (86, 39, 4)
Prechlorinated	7.3-14 (10, 4.5, 2)	19-33 (26, 10, 2)	8.4[a]	105[a]
Sand Filtered	7.3-55 (24, 19, 6)	22-356 (120, 126, 6)	5.1-8.1 (6.2, 1.7, 3)	97-106 (96, 9.9, 3)
Ozonated	8.3-14 (11, 4.3, 2)	22-31 (27, 6.1, 2)	13[a]	82[a]
GAC Filtered	5.7-6.0 (5.9, 0.2, 2)	8.5-9.9 (9.2, 0.9, 2)	<4.2-7.4 (4.7, 2.2, 4)	8.6-35 (22, 13, 4)
Ultrafiltered			7.6[a]	23[a]
Reverse Osmosis			<4.2 (2.1, 0.0, 4)	<1.1-1.3 (0.7, 0.4, 4)
Treated	<4.2-30 (13, 11, 6)	6.9-71 (33, 24, 6)	<4.2-5.5 (3.0, 1.7, 4)[b]	3.0-21 (13, 9.4, 4)[b]

3

4   Conventional treatment (years 2008-2009); advanced treatment (years 2010-2012).

5   [a] Prechlorinated, ozonated and ultrafiltered (n=1).

6   [b] Treated water is a blending of ~50% (conventional treatment) and ~50% (advanced treatment).

7   <LOQ taken as LOQ/2 (2.1 ng/L for PFOA and 0.5 ng/L for PFOS) for statistical calculations (mean and standard

8   deviation).

SUPPORTING INFORMATION

OCCURRENCE OF PERFLUOROOCTANE SULFONATE (PFOS) AND PERFLUOROOCTANOATE (PFOA) IN N.E. SPANISH SURFACE WATERS AND THEIR REMOVAL IN A DRINKING WATER TREATMENT PLANT THAT COMBINES CONVENTIONAL AND ADVANCED TREATMENTS IN PARALLEL LINES.

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Contents of Supporting Information

Table S1: LC-MS/MS parameters established for the H-SRM acquisition mode.

Analyte	precursor ion m/z	TL (V)	quantitation product ion m/z	CE (V)	confirmation product ion m/z	CE (V)
PFOA	413.0	72	369.0	14	169.0	18
PFOS	499.0	110	80.0	55	98.9	54
$^{13}C_4$-PFOA (i.s)	416.8	67	372.0	14	169.0	21
$^{13}C_4$-PFOS (i.s.)	502.8	101	80.0	40	99.0	40
$^{13}C_2$-PFDA (p.s.)	514.9	77	470.0	13	270.0	20

TL: Tube Lens; CE: Collision Energy; i.s.: internal standard; p.s.: performance standard. Scan time: 200 msec.

Fig. S1: Treatment scheme of the DWTP under study.
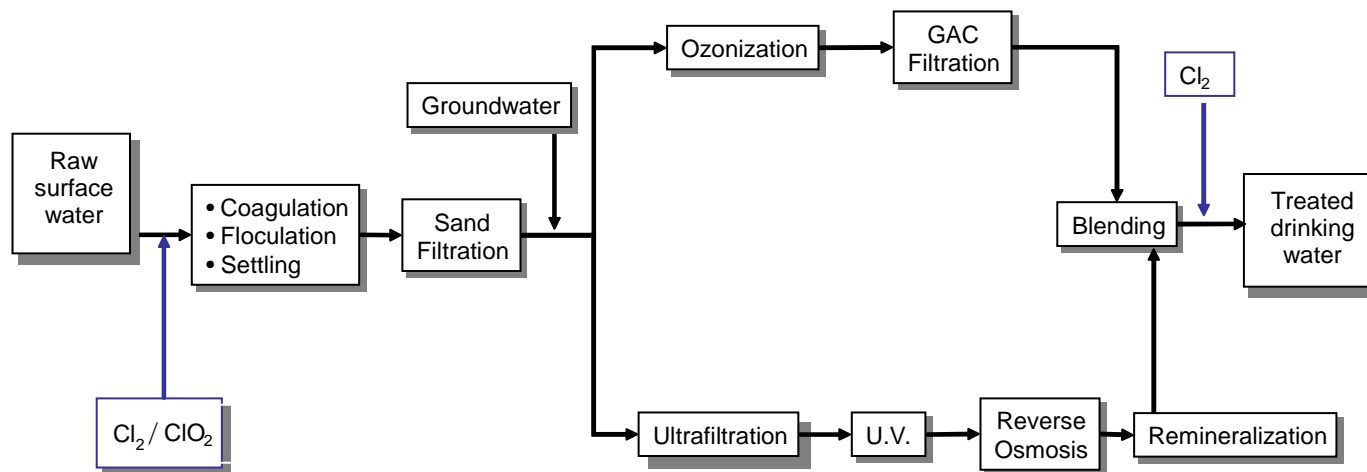
Text S1: Description of treatments in DWTP.

The type of coagulant and the coagulation dose used were PAX-18 at 4 mg/L of aluminum.

The sand filtration flow rate was 3.5 L/(m^{2}s) and each filter had 100 m^2 of area.

Usually 3 mg/L (maximum 5 mg/L) of ozone was used with an average of 30 minutes contact time.

Backwash frequencies employed were 50.000 m^3, approximately once every 2.5 days, for GAC and 15-20 backwashes/day for UF.

GAC is regenerated before it reaches an iodine adsorption coefficient of 450 mg/L. RO concentrates are discharged directly to the Mediterranean Sea.