

# Occurrence and fate of perfluorinated compounds in sewage sludge from Spain and Germany

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**Abstract** Perfluorinated compounds (PFCs) are persistent and bioaccumulative organic compounds used as additives in many industrial products. After use, these compounds enter wastewater treatment plants (WWTP) and long-chain PFCs are primarily accumulated in sludge. The aim of this study was to determine the occurrence and behavior of five PFCs in sludge from 15 WWTP from Spain and Germany that receive both urban and industrial wastes. The PFCs studied were perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA). One gram of freeze-dried, sieved, and homogenized sludge was extracted using an ultrasonic bath with methanol and glacial acetic acid. After that, the extract was recovered and evaporated to dryness with a TurboVap and then 1 mL of acetonitrile was added and the extract was cleaned up with black carbon. Liquid chromatography coupled to mass spectrometry operated in selected reaction monitoring was used to determine target compounds. Quality parameters are provided for the set of compounds studied. PFCs were detected in all samples. In Spanish sludge,  $\Sigma$ PFC ranged from 0.28 to 5.20 ng/g dry weight (dw) with prevalence of PFOS, while in German sludge,  $\Sigma$ PFC ranged from 20.7 to 38.6 ng/g dw and PFBS was the dominant compound. As a next step, the evolution of PFC concentrations within the sludge treatment steps (primary sludge, anaerobic digested sludge, and centrifuged sludge)

was evaluated and differences among levels and patterns were observed and were attributed to the influent water quality and treatment used. Finally, we estimated the amount of PFCs discharged via sludge in order to determine the potential impact to the environment according to different sludge usage practices in the two regions investigated. This manuscript provided an intra-European overview of PFC distribution in sludge. Levels and compound distribution depend on the WWTP sampled. This study demonstrates that PFCs are persistent to sludge treatment and the loads in sludge may pose a future environmental risk, if not controlled.

**Keywords** Perfluorinated compounds · Sludge · Mass loading · Environmental fate

## Background, aim, and scope

Perfluorinated compounds (PFCs) are used in industry and household applications and have emerged as significant global environmental pollutants with persistent, bioaccumulative, and toxic properties. After use or disposal of PFC-containing products, these compounds may enter wastewater treatment plants (WWTP) via industrial or urban waste release (Sun et al. 2011a). Several studies showed that conventional wastewater treatment has a limited efficiency in removing PFCs from aqueous waste streams (Boulanger et al. 2005) and are either accumulated in sludge or released to receiving waters via WWTP effluents (Ma and Shih 2010; Huset et al. 2008; Sinclair and Kannan 2006; Clara et al. 2008). In addition, it was observed that different WWTP from USA exhibited unique distributions of fluorinated alkyl substances despite similarities in the treatment processes (Schultz et al. 2006) and also no consistent trend with respect to the removal of PFCs in seven WWTP from Switzerland were observed (Huset et al. 2008).

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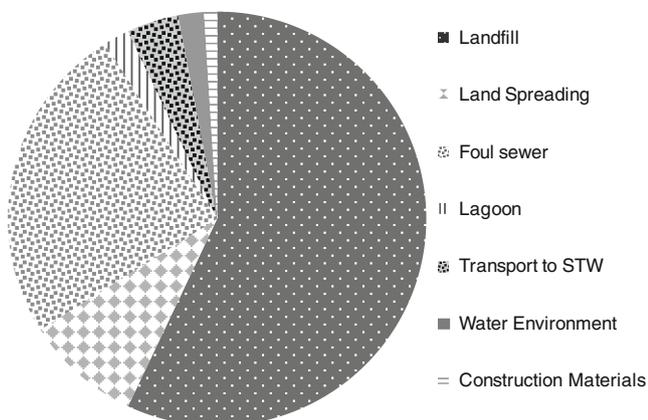
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The EU Council Directive 86/278/EEC specifies parameters to be controlled in sludge previous to its disposal and includes dry and organic matter, metals (cadmium, copper, nickel, zinc, lead, mercury, and chromium), nitrogen, phosphorous, and pH. However, PFCs, as many other organic contaminants, are not legislated in sludge. Nonetheless, their global presence in WWTP sludge suggests the need to control these pollutants to avoid dispersion and contamination of surface water and groundwater (Junling et al. 2011) and/or soils and plants (Hyde 1976; Sanai and Shayegan 1979) via agricultural application.

In Europe, the majority of sludge is disposed to landfills (approximately 57 %), followed by foul sewer and land spreading, among other uses (Fig. 1) (Parsons and Jefferson 2006). Council Directive 86/278/EEC also establishes the minimum requirements and application rates of sludge to agricultural soils. Sludge application to agriculture varies greatly among the various countries. For instance, about 1,065,000 tons of sludge (dry solid) were produced in Spain during 2006, and about 687,000 tons of these was used in agriculture. This is equivalent to 65 % of the total sludge produced (Navarro et al. 2011). In comparison, Germany produced 1,956,447 tons of sludge, of which about 30 % was applied in agriculture (Statistisches Bundesamt Deutschland 2010). However, when any parameter specified in Directive 86/278/EEC exceeds the maximum permissible values, sludge should be incinerated or used for land disposal.

Although there is ample evidence on the accumulation of PFCs in sludge from WWTP in the USA (Loganathan et al. 2007) and China (Guo et al. 2008; Zhou et al. 2010), little is known on the PFC levels in sludge from European WWTP (Sun et al. 2011b) and no data is available on their potential degradability within the sludge treatment steps. In a conventional biological WWTP, water is treated using aerobic digestors where 60–70 % of suspended solids are removed by decantation and produce primary sludge. This primary



**Fig. 1** Possible reported disposal routes for sludge from European WWTP

sludge contains 35 % of the organic matter present in wastewater. Part of this primary sludge is recycled in the water digestors, but the bulk part is stored in anaerobic digestors for 3–4 weeks. In this step, organic matter is reduced, pathogenic bacteria are eliminated, methane is produced, and the overall volume of the sludge is decreased. Finally, sludge is either thermally dried or centrifuged to minimize water content and it is then disposed. Considering that a WWTP generates around 500–1,000 tons of sludge per month, it becomes of primary importance to study the quality of sludge with respect to organic contaminants such as PFCs. The latter serves as a proxy for a multitude of emerging pollutants and new knowledge can help to improve disposal strategies in an environmentally safe and cost-effective way. This includes consideration of available technologies within a WWTP and final use according to the needs of each region and the quality of sludge.

Considering that little information is available on PFCs in sludge from Spain and Germany, the aim of this study was:

1. to compare the levels and compound distribution patterns of PFCs in selected German and Spanish sewage sludge,
2. to evaluate their evolution within the sludge treatment, and
3. to project the loads that are generated in each WWTP and eventually disposed in agriculture.

The data set contains PFC concentration in sludge and will allow a first comparative overview of two countries in Europe that have largely different sludge recycling strategies. Also, it will allow good insight into sources and distribution patterns of PFC that are highly relevant pollutants which so far are not legislated but likely will pose future environmental regulations. Specifically, a limit of 100 ng/g was established for PFCs in sewage sludge used as an agricultural fertilizer in some regions in Germany (e.g., North Rhine-Westphalia and Baden-Württemberg) and PFCs are included in the German Use of Fertilizers Ordinance (German Federal Environmental Agency (UBA) 2009). This is particularly relevant because PFCs have been produced since decades (Ahrens et al. 2009) and, in recent years, environmental concern led to production and disposal alternatives to minimize their impact on the environment.

## Materials and methods

### Chemicals and reagents

Standards of perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexanesulfonate (PFHxS), and perfluorobutanesulfonate (PFBS) were supplied by Wellington Laboratories (Ontario,

Canada). Stock standard solutions were prepared in acetonitrile at a concentration of 5 ng/mL and were stored at  $-18^{\circ}\text{C}$ . Perfluoro-*n*-(1,2,3,4- $^{13}\text{C}_4$ )octanoic acid ( $^{13}\text{C}$ -PFOA) and sodium perfluoro-1-(1,2,3,4- $^{13}\text{C}_4$ )octanesulfonate ( $^{13}\text{C}$ -PFOS), also from Wellington Laboratories, were used as surrogate standards. High-performance liquid chromatography (HPLC) grade water, methanol (>99.9 % purity) and acetonitrile (>99.8 % purity) were purchased from Merck (Darmstadt, Germany) and glacial acetic acid was purchased from Panreac (Barcelona, Spain).

#### Sample collection, preparation, and calculation of mass loads

Both German and Spanish sludge samples originated from WWTP receiving both urban and industrial waters. We have used the inhabitant equivalents as calculated from biodegradable organic load with a biochemical oxygen demand of 5 days of 60 g of oxygen per day as a way to determine the ratio between the loadings derived from industries compared to the amount discharged at the same time by one individual person. In Spain, centrifuged final sludge was collected from 12 WWTP situated in NE Spain (Catalonia, Aragón, and Navarra), with inhabitant equivalents ranging from 17,841 to 835,000. Sampled points are characterized as areas with relatively high population density (Table 1) and high industrial activity related to the textile industry, chemical industry, car industry, and electronic production (Instituto Nacional de Estadística 2011, <http://www.ine.es/welcoing.htm>). These samples are marked as SP1 to SP12 throughout the manuscript.

In Germany, three WWTP (G1, G2, and G3) were located in northern Bavaria in moderately populated areas (105,629, 30,396, and 114,628 inhabitants, respectively) but with relatively large industrial discharge proportions (150,000, 120,000, and 117,000 inhabitant equivalents, respectively), especially G1 and G2. The industrial production ranges from electronic goods to toy manufacturing with hard plastics. In each WWTP, sludge was collected from three sites that follow the passage of waste:

1. primary sludge from biological water tanks,
2. anaerobic digested sludge, and
3. centrifuged sludge.

These samples were analyzed to study the fate of PFCs within the sludge treatment process to test their evolution and changes in concentrations. In each plant, sludge was collected from primary treatment tanks (approximately 95 % water), anaerobic digested sludge (approximately 54 % water), and centrifuged sludge (approximately 20 % water). Precleaned amber jars were used and sludge was stored at  $4^{\circ}\text{C}$  for transport. Characteristics of WWTP including inhabitant equivalents, inhabitants of the nearest city, water influent, treatment type, sludge produced, and final use are indicated in Table 1.

Finally, mass loadings were calculated by multiplying the  $\Sigma\text{PFC}$  concentrations determined in sludge by the monthly production in each WWTP according to Eq. 1:

$$\text{Monthly export} = C_n \times D_n / 1,000 \text{ (g/month)} \quad (1)$$

where  $C_n$  is the  $\Sigma\text{PFC}$  concentration (in nanograms per gram dry weight [dw]) and  $D_n$  is the monthly discharge of sludge (in tons per month) and is divided by 1,000 to convert to grams per month units.

#### Sample pretreatment, extraction, and analysis

Samples were kept at  $-18^{\circ}\text{C}$  and subsequently freeze-dried with an SP Scientific, Virtis Benchtop (Llmenau, Germany). The samples were milled in an agate mortar and sieved to a grain size of 125  $\mu\text{m}$  using a stainless steel screen C.I.S.A., 20 mm diameter  $\times$  50 mm height (Barcelona, Spain). They were further homogenized and kept in amber containers at  $-18^{\circ}\text{C}$  until analysis.

One gram of sample was weighted in polypropylene centrifuge tubes. After the addition of 10  $\mu\text{L}$  of internal standards ( $^{13}\text{C}$ -PFOS and  $^{13}\text{C}$ -PFOA) at a concentration of 5 ng/ $\mu\text{L}$ , samples were incubated for 18 h at  $4^{\circ}\text{C}$ . Nine milliliters of methanol and 10 mL of a 1 % glacial acetic acid solution were then added and the sample was thoroughly mixed using a vortex mixer. Samples were then extracted in an ultrasonic bath for 10 min at room temperature in three extraction cycles with intermediate vortexing. Finally, they were centrifuged at 2,500 rpm for 5 min. The supernatant was transferred to a new vial and evaporated with a TurboVap to dryness. Then, 1 mL of acetonitrile was added to the dried samples and incubated for 10 min in the ultrasonic bath. The samples were then purified by adding 25 mg of activated carbon and 50  $\mu\text{L}$  of glacial acetic acid to 2-mL Eppendorf vials and subsequently vortexed for 1 min. Afterwards, the samples were centrifuged for 10 min at 10,000 rpm. One milliliter of the supernatant was transferred to a clean micro vial. Then, 150  $\mu\text{L}$  of a filtered extract (0.2  $\mu\text{m}$  GHP Accrodisc 13 mm syringe filter, PALL Life Sciences, USA) were dissolved in 350  $\mu\text{L}$  of HPLC grade water.

PFCs were measured using ultra performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS). The system consists of an Acquity UPLC system (Waters, USA) connected to a Triple Quadruple Detector. An Acquity UPLC BEH  $\text{C}_{18}$  column (1.7  $\mu\text{m}$  particle size, 50 mm  $\times$  2.1 mm, Waters, USA) was used as mobile phase residue trap to remove background contamination from the mobile phases. Ten microliters was injected. A LiChroCART HPLC RP-18e column (125 mm  $\times$  2 mm  $\times$  5  $\mu\text{m}$  particle size; Merck, Germany) connected to a  $\text{C}_{18}$  pre-column was used at a flow rate of 0.4 mL/min. The mobile phase was 2 mM  $\text{NH}_4\text{OAc}$  (A)/acetonitrile (B) solution. Gradient elution started at 70 % A and 30 % B and increased to 90 % B in 5 min until 100 % B in 6 s where it was held for 54 s. Initial

**Table 1** Characteristics of WWTP including inhabitant equivalents, influent, treatment type, sludge produced, and final use

WWTP	Inhabitants	Inhabitant equivalents	Water influent (m <sup>3</sup> /day)	Sludge treatment	Tons sludge/month	Sludge use
SP1	12,345	17,841	4,018	Anaerobic digestion and centrifuge	128	100 % compost
SP2	38,930	52,700	12,792	Anaerobic digestion and centrifuge	110	100 % agriculture
SP3	152,641	466,560	103,680	Anaerobic digestion and centrifuge	900	100 % agriculture
SP4	442,308	125,000	56,700	Anaerobic digestion and centrifuge; nutrients removal	605	100 % agriculture
SP5	197,932	90,000	19,992	Anaerobic digestion and thermal dehydration	250	75 % agriculture; 25 % compost
SP6	35,429	78,000	19,000	Aerobic digestion, autoheat, and centrifuge	275	100 % agriculture
SP7	34,432	31,470	6,876	Anaerobic digestion and centrifuge	228	100 % compost
SP8	123,868	451,250	57,000	Anaerobic digestion, thickening, and centrifuge	700	100 % compost
SP9	6,162	108,043	14,062	Anaerobic digestion, thickening, and centrifuge	549	100 % compost
SP10	213,697	350,000	40,000	Anaerobic digestion and centrifuge	933	100 % compost
SP11	207,721	300,000	30,000	Anaerobic digestion and centrifuge	750	100 % agriculture
SP12	973,325	835,000	163,992	Anaerobic digestion and centrifuge	1,350	100 % agriculture
G1 <sup>a</sup>	105,629	150,000	43,358	Primary, anaerobic digestion, and centrifuge	306	75 % incineration; 25 % garden/agriculture
G2 <sup>a</sup>	30,396	120,000	40,000	Primary, anaerobic digestion, and centrifuge	181	100 % incineration
G3 <sup>a</sup>	114,628	117,000	49,200	Primary, anaerobic digestion, and centrifuge	229	33 % incineration; 67 % landfill, landscape

SP Spain, G German

<sup>a</sup> In sludge from Spain, only centrifuged sludge was collected, and for German sludge, primary, anaerobic digested sludge and centrifuged sludge were collected

conditions were kept for 1 min and the system was stabilized for 3 min. PFCs were measured under negative electrospray ionisation and acquisition was performed in selected reaction monitoring using two transitions from parent to product ion to identify each compound (Sánchez-Ávila et al. 2010). Internal standard quantification was performed using <sup>13</sup>C-PFOS to quantify PFOS, PFHxS, and PFBS and <sup>13</sup>C-PFOA to quantify PFOA and PFNA.

#### Quality control parameters

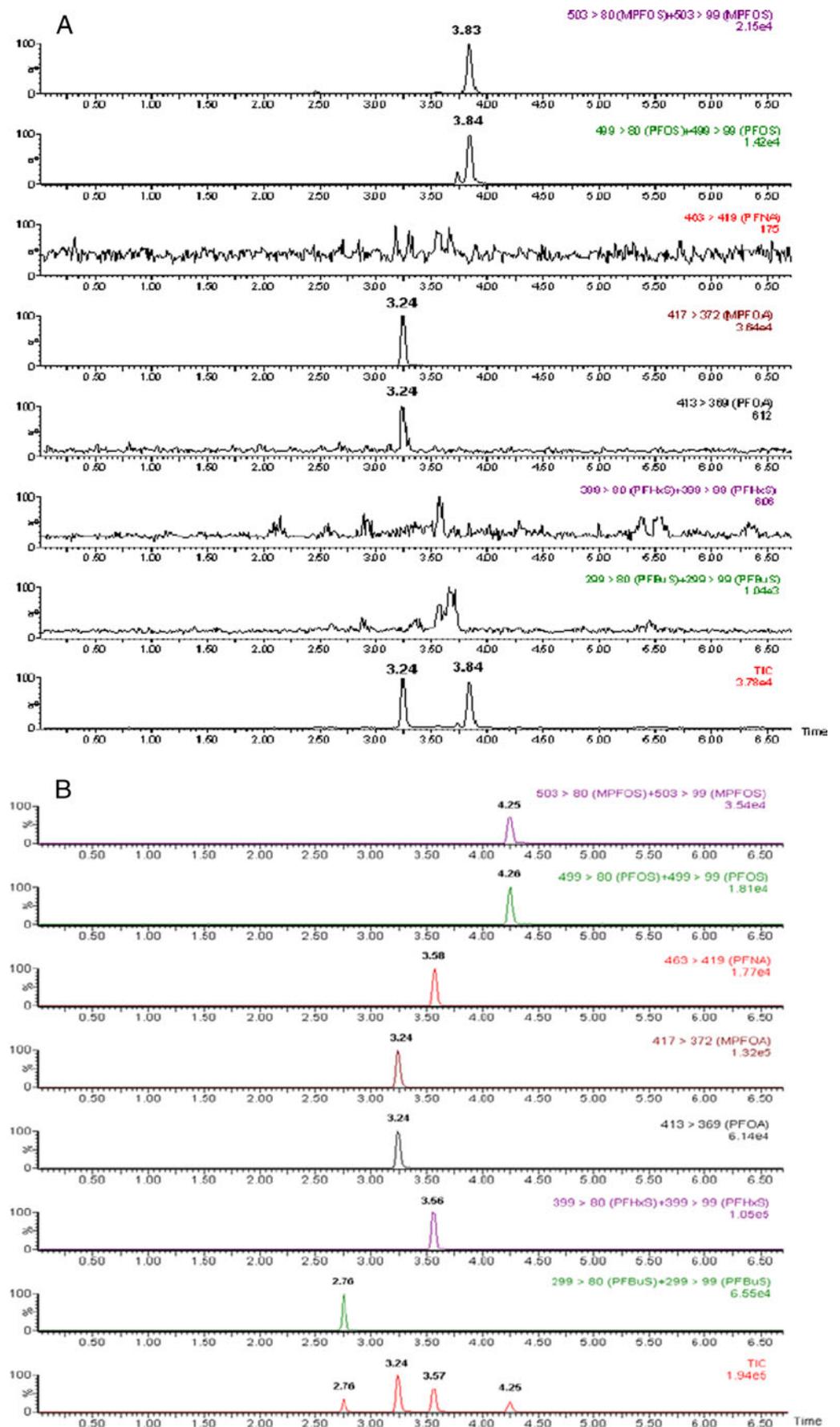
Seven-point calibration curves were prepared at concentration ranges between 2.5 and 100 ng/mL and the method was linear using internal standard quantification with <sup>13</sup>C-PFOS and <sup>13</sup>C-PFOA (correlations of  $r^2 > 0.998$  for all compounds). Instrumental detection limits (LOD<sub>instr</sub>) were determined as the concentration that yielded a signal to noise (S/N) ratio equal or higher than 3. Samples were extracted and analyzed in batches together with a procedural blank in order to monitor external contamination during the whole analytical procedure. No blank contribution was observed neither during extraction nor LC-MS/MS analysis since a column trap was installed previous to the analytical column to avoid PFC contribution

from the LC tubing or mobile phase. Recovery studies were performed in triplicates using unpolluted river sediment spiked with 100 ng/g of both PFC and surrogate labeled standards. Recovery values ranged from 91 to 101 % with relative standard deviation (RSD) between 12 and 23 %. The limit of detection of the method (LOD<sub>meth</sub>) was determined from a spiked sediment sample at an S/N ratio of 3. The performance of the method particularly for sensitivity, selectivity, extraction efficiency, and repeatability of the analysis of

**Table 2** Quality parameters of the HPLC-MS/MS method, percent recoveries (±RSD), and method LOD

Quality parameters	PFOS	PFHxS	PFBS	PFOA	PFNA
Slope	1.81	5.16	2.56	3.84	0.95
$r^2$	0.9991	0.9992	0.9982	0.9994	0.9998
LOD <sub>instr</sub> (pg)	0.12	0.05	0.08	0.08	0.27
Percent recoveries ±RSD, $n=3$	94±17	91±18	100±23	93±15	101±12
LOD <sub>meth</sub> (S/N=3), ng/g dw	0.12	0.05	0.05	0.10	0.14

**Fig. 2** HPLC-MS/MS chromatogram of a sludge sample SP5 (a) and a standard solution at 25 ng/mL (b)



PFCs in sludge is shown in Table 2. Figure 2 shows two LC-MS/MS chromatograms of sample SP5 and a standard solution at 25 ng/mL. These chromatograms show that extraction and analytical methods were suitable and that there were no matrix interferences.

## Results and discussion

### PFC patterns in Spanish and German sludge

PFCs were detected in all sludge samples. In sludge from Spain, the  $\Sigma$ PFCs was between 0.28 and 5.20 ng/g dw, much lower than those found in sludge from Germany, with  $\Sigma$ PFCs between 20.7 and 38.6 ng/g dw (Table 3). Overall, if compared to PFC values in sludge from other parts of the world, the concentrations in the studied samples are quite low, suggesting that urban and industrial sources are not significant. PFC differences between sites can be attributed to the urban activity (inhabitant equivalents) as a measure of industrial/urban inputs and water inflows, which—together with the WWTP design—are the main factors that contribute in the quantity and quality of sludge generated. Against expectation, no correlation was observed between individual or  $\Sigma$ PFCs with inhabitant equivalents, inhabitants, and water inflow or tons of sludge produced in the studied WWTP. Contrarily, there is a very good correlation between inhabitant equivalents and water inflow ( $r^2=0.8162$ ) and between inhabitant equivalents and sludge produced ( $r^2=0.847$ )

when considering the 15 WWTP investigated from Spain and Germany (Fig. 3). Because consumer products seem to be another important source of PFCs to WWTP, we evaluated possible relationships between PFC concentrations and population in the WWTP catchment and no relationship was observed. On the contrary, some correlations were observed between inhabitants and water inflow ( $r^2=0.693$ ) and between inhabitants and sludge produced ( $r^2=0.570$ ), indicating that inhabitant equivalents is a better descriptor of pollution loads in a specific WWTP. This means that initial water disposal management carried out in each area plays an important role in the PFC accumulation in sludge within a WWTP.

In Spain, sludge from SP5, SP10, SP11, and SP2 had the highest  $\Sigma$ PFC concentrations among samples, with 5.20, 4.46, 3.93, and 3.15 ng/g, respectively. All these places have contributions from industrial sectors with vehicle, textile, and chemical industries. On the other hand, the samples with the lowest levels correspond to agricultural sites with little population and industrial pressure. In contrast, the highest PFC concentration in sludge from southern Germany (G1, G2, and G3) was in sample G3, with  $\Sigma$ PFCs of 38.6 ng/g dw. The other two sludge samples had similar  $\Sigma$ PFCs. A plausible source for PFCs is hard plastic production for instance from influences of the toy industry in this area. Other specialized industries such as production of office material might also contribute to these high values.

Overall, the levels found in WWTP of both Germany and Spain were low compared to other regions, especially Asia

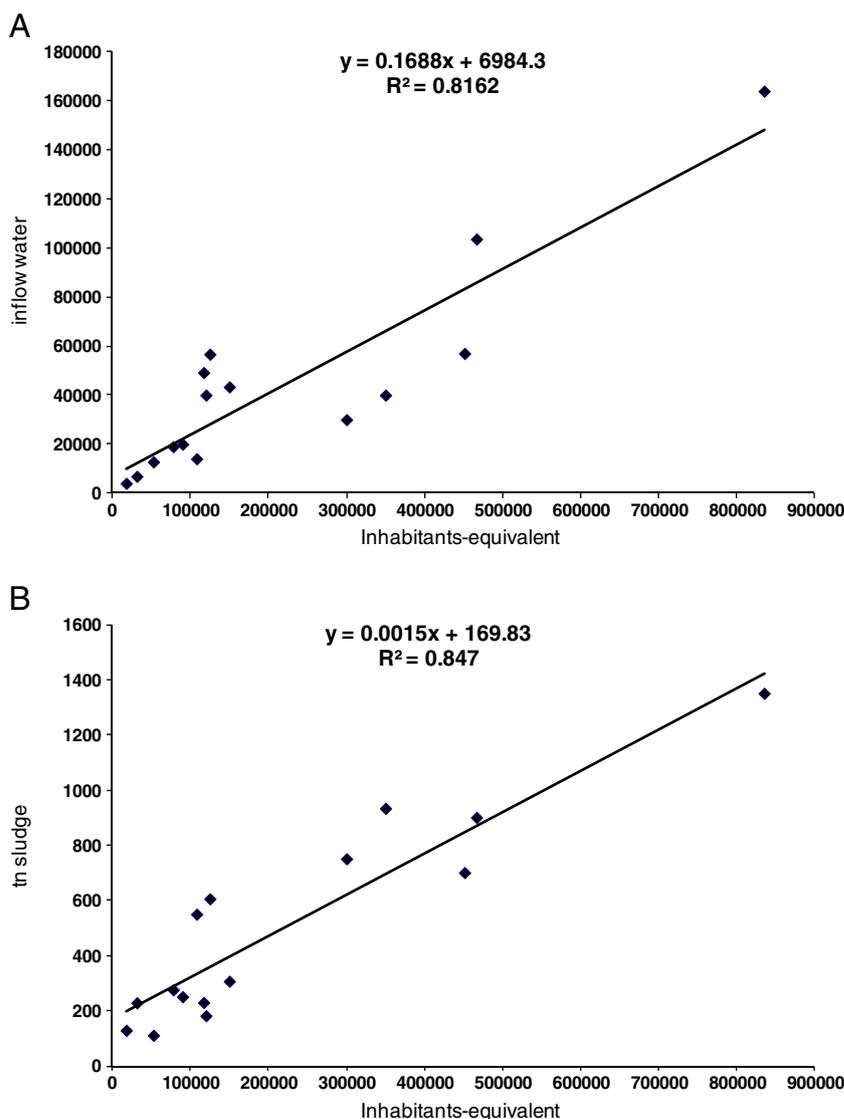
**Table 3** Levels of PFCs (in nanograms per gram dw) in Spain and German sludge

	Concentration of PFCs (ng/g)					$\Sigma$ PFCs	Mass loadings (g/month)
	PFOS	PFHxS	PFBS	PFOA	PFNA		
Spain sludge							
SP1	1.91	BDL	BDL	0.48	0.29	2.68	0.34
SP2	2.77	BDL	BDL	0.21	0.17	3.15	0.04
SP3	1.96	0.10	BDL	BDL	BDL	2.06	1.85
SP4	0.28	0.10	BDL	0.12	BDL	0.50	0.30
SP5	4.99	0.05	BDL	0.16	BDL	5.20	19.2
SP6	BDL	BDL	BDL	0.08	0.20	0.28	0.01
SP7	0.68	BDL	BDL	0.22	BDL	0.90	0.20
SP8	0.76	BDL	BDL	0.19	BDL	0.95	0.07
SP9	0.54	BDL	0.11	0.21	0.89	1.75	0.97
SP10	2.84	BDL	BDL	0.58	1.04	4.46	2.68
SP11	1.40	BDL	1.84	0.69	BDL	3.93	2.75
SP12	0.68	BDL	0.14	BDL	BDL	0.82	1.11
German sludge							
G1	4.45	1.06	7.89	0.95	6.36	20.7	6.33
G2	2.08	1.04	12.9	0.59	4.19	20.8	3.76
G3	3.73	1.40	29.1	1.21	2.40	38.6	8.84

These values correspond to the final centrifuged sludge

BDL below detection limit

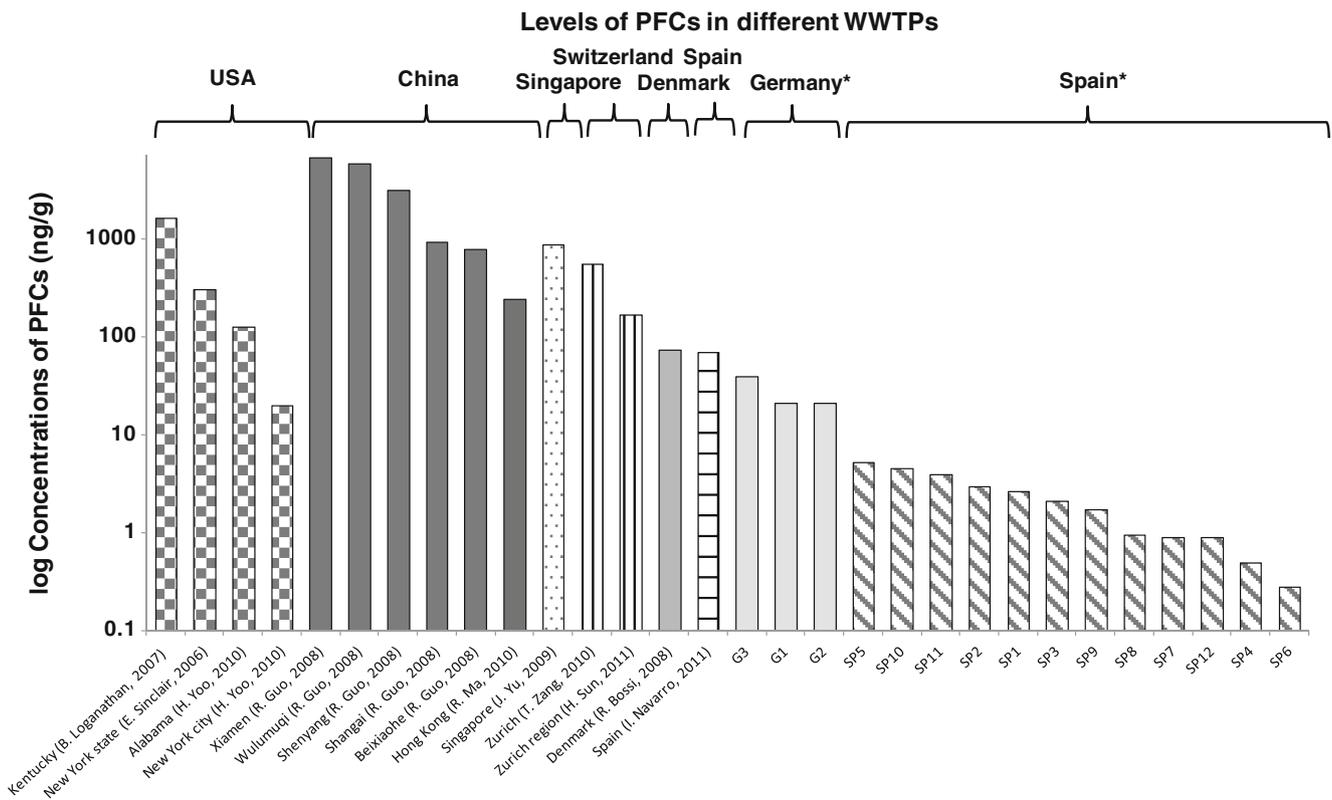
**Fig. 3** Correlation graphics (a) inhabitant equivalent vs inflow water and (b) inhabitant equivalent vs tons sludge) of 15 WWTP studied



where industrial inputs to WWTP can be much higher. A study carried out in February 2004 to determine the presence of PFCs in sludge from 16 WWTP from China reported  $\Sigma$ PFC values 1,000 times higher than those of the present study, with 926 ng/g in sludge from Shanghai, 3,132 ng/g in Shenyang, and 6,622 ng/g in Xiamen (Guo et al. 2008). Furthermore, Yu et al. (2009) reported 884.3 ng/g in sludge from a Singapore WWTP attributed to the 1,700,000 inhabitant equivalents and a water inflow of  $361 \times 10^6$  L/day (corresponding to 95 % domestic wastewater and 5 % to industrial wastewater) (Yu et al. 2009). In another study, three sewage sludge samples from near Zürich were analyzed and levels of  $\Sigma$ PFCAs and PFOS with methanol extraction were of 14.6 and 176 ng/g, respectively, in Horgen WWTP with 20,560 inhabitant equivalents ( $11.9 \times 10^6$  L/day), 17.9 and 383 ng/g, respectively, in Wädenswil WWTP with 19,000 inhabitant equivalents ( $17.2 \times 10^6$  L/day), and 23.8 and 1,121 ng/g, respectively,

in Dübendorf WWTP with 37,000 inhabitant equivalents ( $21 \times 10^6$  L/day) (Zhang et al. 2010). In another study,  $\Sigma$ PFCs of 1,620.5 ng/g were detected in sludge from a WWTP of Kentucky (Loganathan et al. 2007) with domestic and commercial wastewater from 150,000 inhabitant equivalents and an industrial inflow of  $19.7 \times 10^6$  L/day. Figure 4 compares the  $\Sigma$ PFCs levels in sludge from the various sites described above.

For specific compound distribution, PFOS accounted for 31 to 96 % of  $\Sigma$ PFCs in Spanish sludge. A previous study suggested that PFOS can originate from biotransformation of *N*-ethyl-*N*-(2-hydroxyethyl)perfluorooctanesulfonamide (Higgins et al. 2005). Volatile precursors of PFOS may be another potential source of pollution (Guo et al. 2008). In comparison to PFOS, PFOA had concentrations that ranged between 1.08 ng/g (SP9) and 0.69 ng/g (SP13). They stem from WWTP that are likely related to areas with manufacturing of fluoropolymers such as Teflon® and



**Fig. 4** Comparative graph showing the levels of PFCs (in nanograms per gram dw) in sludge from several WWTP around the world. Asterisks denote samples analyzed in this study

semiconductors (Lin et al. 2009). All samples had PFNA contents that were much lower than PFOS and PFOA. Furthermore, some of the compounds investigated such as PFHxS and PFBS were only detected in four samples. Our results in Spain match nicely with those of Navarro et al. (2011). These authors found levels of PFCs between 0.01 and 286.81 ng/g with PFOS as the dominant compound detected in sludge collected in 2010 from different WWTP from Spain (Navarro et al. 2011). Similar findings were published by Pan et al. 2011, who found PFOS as the dominant compound in sludge from China with a contribution of 79 % of  $\Sigma$ PFCs analyzed (Pan et al. 2011).

In German sludge, PFBS showed the highest levels with values ranging from 7.89 to 29.1 ng/g dw. This was followed by PFNA (from 2.4 to 6.36 ng/g dw) and finally PFOS (from 2.08 to 4.45 ng/g dw). In particular, PFOS has been used during the past six decades, but in 2001, the multinational company 3 M decided to phase out its production in favor of other PFCs such as the PFBS. Possibly, the higher usage of 3 M materials may have triggered the increase of PFBS in Germany; however, this hypothesis is difficult to confirm. In Germany, PFC in sludge seem to show a decrease in recent studies (<http://www.um.baden-wuerttemberg.de/servlet/is/63509/> and <http://www.um.baden-wuerttemberg.de/servlet/is/82635/>), although accumulative enrichment of sludge

application may still be a reality when projecting applications over the last years to decades. In addition, cumulative loading may also be a concern for new persistent compounds that may substitute conventional PFC.

#### Fate of PFCs within the sludge treatment process

So far, the turnover and accumulation of PFCs in WWTP have hardly been characterized or quantified. This study shows the first data of PFC concentration changes along the sludge treatment pathway, starting from the primary sludge input via the anaerobic bioreactor towards the sludge dewatering process by centrifugation. This is important because, next to costs of disposal, pollutant loads decide the potential use of sludge, for instance in agriculture. Dioxins and furans (Li et al. 2011), polycyclic aromatic hydrocarbons (Zhai et al. 2011), and alkylphenols (Fernández-Sanjuan et al. 2009) have been explored for final organic contaminant loads in sludge; however, little is known for PFCs in this context.

Figure 5 shows the concentration levels of PFCs within the sludge treatment pathway of three WWTP of Germany. Sample G1 contained  $\Sigma$ PFC of 56.0 ng/g dw in primary sludge and PFBS was the main contributor. The levels of PFBS were lower in anaerobic digested sludge and centrifuged sludge and suggest degradation under anaerobic conditions (Parsons et al. 2008). The presence of PFOS and

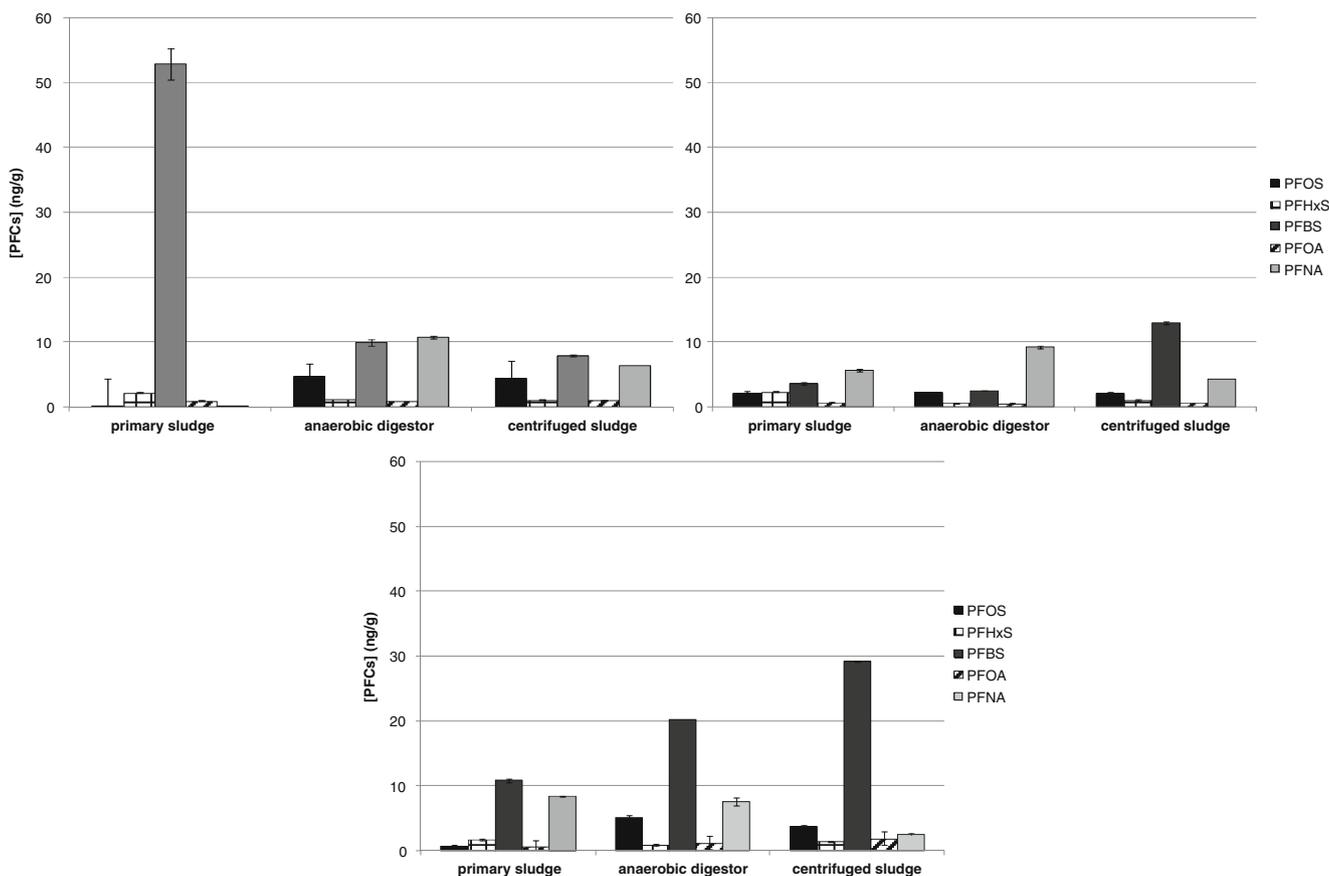


Fig. 5 Bar chart of individual PFC compounds within the sludge treatment pathway in Germany WWTP

PFNA in anaerobic digested sludge and centrifuged sludge compared to primary sludge may be caused by the degradation of 2-(*N*-ethylperfluorooctane sulphonamide)acetic acid which could generate PFOS during sludge treatment (Higgins et al. 2007). The patterns of PFCs in G2 and G3 were similar, with PFBS, PFNA, and PFOS being the main contributors to  $\sum$ PFCs and showing variations in concentration which reflect the treatment and influent water quality of each WWTP.

The different PFC levels in primary sludge, anaerobic digested sludge, and centrifuge sludge of G1, G2, and G3 are related to hydraulic residence times, the duration of digestion in the bioreactor, and the dewatering technique. Typically, the raw sewage passes through primary treatment within a matter of hours, while the bioreactor accumulates sludge over several weeks (normally 3 to 4 weeks). This means that small concentrations found in the raw sewage stage can be more arbitrary due to daily or even hourly variances. The reverse is also true for high pollutant contents in the G1 primary sludge when compared to the anaerobic digester. It means that concentration differences between primary sewage and anaerobic digested sludge are poor indicators for degradation unless high-frequency sampling is established for several weeks. The results of this study hint at the possibility that PFCs are not removed

during sludge treatment and are transferred within the sludge treatment line until finally disposed. It reflects a generally problematic stage that new methods for the removal of PFCs from sludge have to be further developed.

#### Mass loadings

Because of the high organic content of sludge, sewage sludge has valuable agronomic properties and is applied as fertilizer in many countries. The use of sewage sludge must take into account the nutrient needs of plants, but should not compromise the quality of the soil or surface water and groundwater (Fytli and Zabaniotou 2008). Mass loads of PFCs were calculated according to Eq. 1 using the  $\sum$ PFC concentration and the sludge generated in each WWTP (Tables 1 and 3). Calculations were performed on a monthly basis because sludge was collected from anaerobic digested sludge (with several weeks of residence time) and centrifuged sludge. The maximum  $\sum$ PFC load found in this study was 8.84 g/month (G3), while the minimum was 0.01 g/month (SP6). Only few studies report PFC accumulation in sludge during the wastewater treatment processes and mass loads. In Thailand, Kunacheva et al. (2011) found that WWTP were largely ineffective in removing PFCs by the activated sludge and that 3307 mg of PFOS were

accumulated in sludge per day. In Korea, the emission rates of PFCs ranged from 0.59 to 1.03 tons/year (49,166 to 85,833 g/month) when taking into account the total production of domestic and industrial wastewaters (Kim et al. 2011).

Considering the different rates of agricultural use of sludge (65 % of all produced sludge in Spain and 30 % in Germany), these mass accumulations may have significant effects on soils. The severity of impact depends on the area the sludge is spread upon. In Germany, 1.66 tons of sewage per hectare are allowed per year and the maximum annual load from this data set would mean a PFC load of 3.69 mg/m<sup>2</sup>/year. While this amount seems negligible, one has to consider the poor degradability of the compounds. With this, accumulation over decades can easily multiply this amount. In other countries, higher sludge applications to agriculture might produce increases in the PFC loadings to soils. For instance, Bulgaria has an allowed spreading rate of 55 tons/ha/year, while Spain has no regulations for maximum sludge applications (Milieu 2011). However, Spanish legislation ensures the observance of the limit values for the quantities of metals introduced into soils per unit of area and unit of time.

Application of sludge in agricultural soils may lead to the dispersion of PFCs. In Alabama, USA, PFCs were detected in sludge-amended soils from 320 to 410 ng/g, much higher than untreated soils, and a low mobility of longer-chained compounds was observed (Washington et al. 2010). A recent study found that PFOS > PFOA > PFDoA > PFHpA > PFHxA in soils from the USA, China, Japan, Norway, Greece, and Mexico at 0.5 to 79.1 ng/g dw and suggest that waste disposal of WWTP effluents or biosolids on soils can be the main cause of contamination (Strynar et al. 2011). Another study investigated the occurrence and fate of PFCs by evaluating the levels, mass balance, desorption, and transport of PFCs in soils receiving application of municipal sludge at various loading rates. PFOS was the dominant PFC in both sludge (80–219 ng/g) and sludge-amended soil (2–483 ng/g) (Sepulvado et al. 2011). PFCs accumulation in soil and leaching to groundwater and subsequent transport to other ecosystems such as rivers and lakes might also constitute a threat to the environment. The environmental and health effects are so far poorly characterized; however, this finding provides a good example for micro-pollutant spreading to the environment via sludge.

## Conclusions

PFCs have been detected in sludge from 15 differently operating WWTP situated in Germany and Spain at concentrations and patterns that best reflect the activities carried out in each region. In addition, our results suggest that PFCs persist within sludge treatment pathways (from primary sludge to centrifuged sludge). On the contrary, increases towards the end of the treatment pathway may result from degradation of precursor materials. Different sludge residence times in the reactors and dewatering

techniques determine the evolution of PFCs within the sludge treatment process. Considering the variable amounts of sludge generated in WWTP, its use in agriculture may be particularly critical for sludge with moderate to high PFC concentrations. Even low concentrations may become a concern when cumulative loading takes place over many years. This manuscript provided an overview on PFC distribution in sludge and may serve as a good comparative overview for other pollutants generated in industrial processes that may have similar persistence. Future work should consider potential industrial sources in the catchment and the possibility of discontinuous inputs of the chemicals into the aquatic environment. Studies of this sort should also include higher-frequency monitoring, particularly of the raw sludge input in order to resolve concentration differences between treatment steps within WWTP.

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