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Review

Pathways and factors for food safety and food security at PFOS contaminated sites within a problem based learning approach

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Abstract

Perfluorooctanesulfonic acid (PFOS) and related substances have been listed in Annex B of the Stockholm Convention. The implementation requires inventories of use, stockpiles, and environmental contamination including contaminated sites and measures for (risk) reduction and phase out. In most countries monitoring capacity is not available and therefore other approaches for assessment of contaminated sites are needed. Available informations about PFOS contamination in hot spot areas and its bio-accumulation in the food webs have been merged to build up a worst-case scenario We model PFOS transfer from 1 to ~~–~~100 ng L^{-1} range in water to extensive and free-range food producing animals, also via the spread of contaminated sludges on agriculture soils. The modeling indicates that forages represented 78% of the exposure in ruminants, while soil accounted for >80% in outdoor poultry/eggs and pigs. From the carry-over rates derived from literature, in pork liver, egg, and feral fish computed concentration falls at 101, 28 and 2.7 ng g^{-1}, respectively, under the 1 ng L^{-1} PFOS scenario. Assuming a major consumption of food produced from a contaminated area, advisories on egg and fish, supported by good agriculture/farming practices could abate 75% of the human food intake. Such advisories would allow people to become resilient in a PFOS contaminated area through an empowerment of the food choices, bringing the alimentary exposure toward~~s~~ the current Tolerable Daily Intake (TDI) of 150 ng kg^{-1} body weight d^{-1} proposed by the European Food Safety Authority (EFSA).

Abbreviations: bw, body weight; dm, dry matter; EFSA, European Food Safety Authority; fw, fresh weight; MOS, margin of safety; OC, organic carbon; PFAS, poly- and per-fluorinated alkyl substances; PFCAs, perfluorinated alkyl carboxilic acids; PFOS, perfluorooctane sulfonic acid; PFSAs, perfluorinated sulfonic acids; TDI, tolerable daily intake; US EPA, Environment Protection Agency of the United States; WWTP, waste water treatment plants

Keywords: PFOS; H~~h~~ot spot; F~~f~~ood safety; F~~f~~ood security; I~~i~~ntake; E~~e~~mpowerment

1 Introduction

Perfluoroalkane sulfonic acids (PFSAs) and ~~Perfluoroalkyl~~ perfluoroalkyl carboxylic acids (PFCAs) are highly persistent chemicals with a toxicological characterization continuously in progress (Joensen et al., 2009; Stahl et al., 2009; Lindstrom et al., 2011; Bull et al., 2014). Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and other long-chained PFSAs (with 6 or more perfluorinated carbons) and PFCAs (with 7 or more perfluorinated carbons) bioaccumulate and biomagnify despite their water solubility (Martin et al., 2004; Conder et al., 2008). Therefore, in May 2009 perfluorooctane sulfonate (PFOS) and PFOS related substances were listed as the first PFAS in the Stockholm Convention as Persistent

Organic Pollutant (POP~~s~~) (Stockholm Convention, 2011, 2012), to be addressed globally within the management frame of the Convention. Now, many of the 179 countries which are parties to the Convention have started to establish inventories for PFOS use, stockpiles and environmental contamination including contaminated sites. The largest PFOS production and use took place between 1980 and 2001 with a production volume of approx. 4~~,~~500 t yr^{-1} (Paul et al., 2010). After 3 M stopped the PFOS production the volume dropped dramatically to approximately 100~~to~~–200 t production after 2002 with production volume largely in China (Lim et al., 2011; Zhang et al., 2012) and minor production in Germany and Italy (Oliaei et al., 2013). Therefore, in addition to managing current production and use (European Parliament, 2006), the major management task to appropriately address PFOS are remaining stockpiles and the legacies of the historic production and contaminated sites along the life cycle (Stockholm Convention, 2011). This includes the pollution from (former) production sites (Oliaei et al., 2013; ~~Wang et al., 2010;~~ Bao et al., 2011; ~~d~~D'Hollander et al., 2011) but also sites where PFOS has been used in productions (e.g. chromium plating, paper or textile impregnation industries). One important sink of PFOS and long chain PFCAs were/are here the industrial sludges and municipal sewage sludge recovered from contaminated influents: the PFOS coefficient of absorption to the organic carbon makes sludges and derived biosolids 3 order of magnitude more contaminated than the influent water (Arvaniti et al., 2014). The application of such PFSAs/PFCAs containing sludges as “bio-solids” has resulted in contaminated areas and some of the sludge application impacted pasture land (Skutlarek et al., 2006; Wilhelm et al., 2008; Lindstrom et al., 2011; Oliaei et al., 2013). Furthermore, the use of firefighting foams has resulted in many PFOS contaminated sites at firefighting practice areas and areas with fire incidents where PFOS containing foams have been used (Moody and Field, 2000; Weber et al., 2010; Houtz et al., 2013). Due to their water solubility, PFOS and other long chain PFSAs and PFCAs are mobilized and released from landfills in water bodies as consequence of the progressive saturation of the binding sites linked to the organic matter of the soil (Huset et al., 2008, 2011; Busch et al., 2010; Weber et al., 2011). The Stockholm Convention inventory guidance for PFOS includes therefore a dedicated chapter on the inventory of PFOS contaminated sites (Stockholm Convention, 2012). One challenge of the Convention implementation is that developing countries have hardly any analytical capacity for PFOS and other per- and poly-fluoro alkyl substances (PFAS) and only a limited amount of studies reported on PFOS levels in developing countries but measured in industrial countries (Guruge et al., 2005; Orata et al., 2009; Sindiku et al., 2013). To our knowledge no study has investigated PFOS/PFAS such sites in developing countries. However, from risk assessment perspective the affected population at particular contaminated sites might show exposure levels higher than the TDI of 150 ng kg^{-1} bw d^{-1} set by EFSA for PFOS (EFSA, 2008). Locally produced and consumed food of animal origin may play a relevant role in determining potential over-exposures with respect to such guidance value, as matter of the bioaccumulative behavior of PFOS and of the food consumption habits of the target population. Within a comprehensive risk assessment for human health, it seems mandatory to include all potential food exposure pathways (Oliaei et al., 2013), as far human intake might not acknowledge feral fish and drinking water only as the major contributing food items in a hot spot area (Minnesota Health Department, 2008). Owing to the above, in this paper we aimed to exploit the driving questions arising from the health-based risk management option in a potential emblematic PFOS hot spot rural area. One goal is to provide policy makers and risk managers a PFOS exposure scenario which includes the major pathways and known factors that may play a pivotal role in enhancing or mitigating rural community PFOS food intake in contaminated site and the current state of knowledge on fate and bioaccumulation of PFOS in the food webs. Such a summary of food-related exposure pathways, bioaccumulation factors and carry-over rates might be beneficial in particular for countries without analytical capacity and limited monitoring options. More in general, a cost-effective risk-oriented approach would consist on enabling communities to become PFOS-resilient in a contaminated area through an empowerment of their local water and food choices (WHO Regional Office for Europe, 2013).

2 Materials and methods

2.1 Description of a worst case scenario

The PFOS worst-case scenario have been built up by merging the available informations about contamination linked to hot spot areas (~~d~~D'Hollander et al., 2011, 2014; Stahl et al., 2012; Oliaei et al., 2013; Polesello and Valsecchi, 2013). An organo-fluorochemical industry with a longer history with Electro Chemical Fluorination (since 1980) for the synthesis of PFOS and other PFAS is settled in a critical geological area for the presence of an undifferentiated aquifer with its recharge area. Such aquifer represents the main water reservoir for a large part (about 150 square km) of a downhill plain almost devoted to agriculture and animal farming practices. The improper disposal of industrial sludges and effluents from the production process was the main reason for the PFOS contamination of the aquifer. The pollution levels range ~~from~~ from <10 ng L^{-1} up to 100 ng L^{-1} both in surface and ground water. Water-line and ground wells are both used for tap water supply in different towns of the district. Plenty of water-table private wells supply water to small communities and farms with courtyard animals. Biosolids from the sludges of municipal wastewater treatment plants impacted by the pollution in the area have been regularly spread since more than ~~ten~~ 10 yrs on agriculture soil as top soil improvers and fertilizers. Average sludge application rate on croplands (wheat and maize) and pasture was/is of 5.0 t ha^{-1} yr^{-1}, equivalent to 31 t ha^{-1} yr^{-1} of a mixed compost (16% of sludge), in horticulture. The impacted area is characterized by the presence of small rivers and ponds allowing fishing and the use of surface water in agriculture. Boars' hunting is practiced to limit the boar community as potential invasive species for crops, and the boar meat is regularly placed on the market, after veterinary inspections. Small scale animal farming practices account for the local production of forages, administered to food producing animals (Fig. 1).

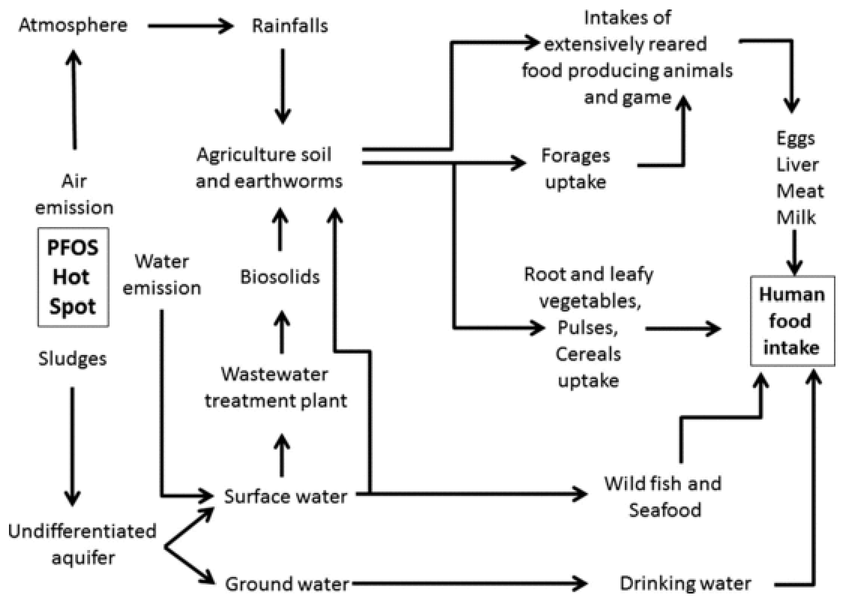

Fig. 1 Diagram of the inventoried pathways leading to alimentary exposure in the considered hot spot scenario characterized by the PFOS contamination of an undifferentiated aquifer.

2.2 Modeling the transfer of the PFOS contamination from the water cycle and soil to products of animal origin

In hot spot areas, food producing animals may be exposed to PFOS via drinking water, and via the intake of top soil and forages harvested from contaminated soils as consequence of the agriculture use of sludges from wastewater treatment plants. The direct intake of PFOS from contaminated water in farmed animals has been calculated considering the recommended water supply to satisfy animal welfare parameters (Rossi and Gastaldo, 2005). Estimates of top soil intake for the free-range livestock were derived from the European Food Safety Authority opinion (EFSA, 2011) on persistent organic pollutants intake in small ruminants (6% of the dry matter intake from forages), from Edwards (2003) for pigs (20%), and from Waegeneers et al. (2009) for poultry flocks (50%), as consequence of animals grazing behavio~~u~~r on amended pastures and soils (Table 1). To this purpose, expected concentration of PFOS in sludges from WWTPs have been derived using the accumulation factor with respect to that in water influents (~~*~~×3~~,~~050) as reported by Yoo et al. (~~2009~~2010). According to Sepulvado et al. (2011) it was then possible to model the occurrence of PFOS on agriculture soils and pasture as consequence of the regular land application of municipal biosolid, through the equation: $y = 0.896x + 0.423$. The transfer factor from contaminated soil to forages was derived from Yoo et al. (2011) for hay from grass (~~*~~×0.25, as average for PFOS and PFOA and from Stahl et al. (2013) for mais silage (~~*~~×0.17), on dry matter basis (Table 2). Therefore, for dairy and beef animals, it was possible to estimate the PFOS intake, expressed as ng kg^{-1} body weight (bw) d^{-1}, accounting for the default animal nutrition and production parameters reported in Table 1.

Table 1 Animal production parameters considered for the proposed model, along with the forage and soil intake.

Animal	Weight (kg bw)	Water intake[a] (L d~~ay~~$^{-1}$)	Forages intake (silage + hay) (kg dm d^{-1})	Soil intake (kg dm d^{-1})	Product
Dairy cow	500	97	8 + 6	2.8[c]	Milk 23 kg d^{-1}
Dairy sheep	60	8	1.2 + 0.8	0.40[c]	Milk 1.6 kg d^{-1}
Fattening bull	450	60	5 + 3	1.6[c]	Meat burden 270 kg
Fattening pig	110	10	0.5 + 2.5[b]	0.60[c]	Meat burden 66 kg
Broiler	2.5	0.5	0.1[b]	0.05[c]	Meat burden 1.8 kg
Laying hen	3.5	0.5	0.12[b]	0.06[c]	Egg 50 g d^{-1}

[a] Water consumption estimated at +23 °C.

[b] Referred to grains and commercial feeds.

[c] Conservative soil intake scenario (20% of forages dry matter intake for mammalian species, 50% for poultry).

Table 2 Modeled concentrations in sludge, digestate, top soil amended with sludge and digestate, and forage (ng g^{-1} dm) considering PFOS concentration (ng L^{-1}) in influents at municipal waste water treatment plants.

Influent (ng L^{-1})	Sludge (Yoo et al., ~~2009~~2010)	Digestate (Yoo et al., ~~2009~~2010)	Top soil (Sepulvado et al., 2011)	Hay (Yoo et al., 2011)	Mais silage (Stahl et al., 2013)
1	3.050	5.338	2.580–4.516	0.645–1.129	0.439–0.768
5	15.25	26.69	12.90–22.58	3.225–5.645	2.193–3.839
10	30.05	53.38	25.80–45.16	6.451–11.29	4.387–7.677
25	76.25	133.4	64.51–112.9	16.13–28.22	10.97–19.19
50	150.0	266.9	129.0–225.8	32.25–56.45	21.93–38.38
75	228.7	400.3	193.5–338.7	48.38–84.67	32.90–57.58
100	305.0	533.8	258.0–451.6	64.51–84.67	43.87–76.77

2.3 Carry-over rates

Accounting for the modeled animal exposure (ng kg^{-1} bw d^{-1}) via water, forages, and top soil, the correspondent concentration in edible tissues (muscle, liver, milk) was derived from animal toxicokinetics data of feeding trials with contaminated grass silage and hay reported in sheep and cow by Kowalczyk et al. (2012, 2013), and from the observational study in dairy cows by Vestergren et al. (2013). Carry-over rates (COR), as ratio between the total amount of PFOS in the tissue/milk of the considered farmed species and the total amount ingested by the animal were derived from the sheep study for liver (9.1), and muscle (11.6). For bovine milk, the Bioconcentration Transfer Factor (BCF = log ~~-~~ −1.67) from Vestergren et al. (2013) was selected, because referred to a standard farming management of dairy animals. The default body and organ burdens, and milk yields shown in Table 1 were assumed to convert intakes (ng kg^{-1} bw d^{-1} into ng g^{-1} of food contamination). For broilers, Yeung et al. (2009) reported an averaged blood concentration of 1~~,~~890 ng mL^{-1} in chickens daily exposed by gavage to 0.1 mg kg^{-1} bw dose of PFOS. Accounting for a 5% burden of blood, and a 70% burden of muscle tissue on the body weight, this would result in a factor of 1.1 to correlate the dose with muscle concentration of PFOS. For farmed pigs, toxicokinetics parameters were derived from Numata et al. (2014) who reported a Biomagnification Factor (BMF) equal to an arithmetic mean of 10.4 ± 8.4 as standard deviation in meat and 503 ± 332 in liver, with respect to the contamination of the feed on dry matter basis. Because the large dispersion around the BFM, the application of the arithmetic mean of BMFs to low doses PFOS intake in pigs would lead to model~~l~~ed contamination in meat and liver somewhat 10–100 fold higher than those reported in such food matrices from market investigations (Hlouskova et al., 2013). To be consistent with the contamination levels determined in pork meat and liver from not hot spot areas, the above arithmetic mean BMF values were corrected by subtracting 1 sd; theoretical feed contamination was recovered by dividing the model~~l~~ed amount of PFOS intaken in a 110 kg ~~-~~bw pig by 3.0 kg of feed (Table 1). For laying hens, egg contamination was derived directly from that of soil, considering a factor of 8.9 reported by ~~d~~D'Hollander et al. (2011) in Flemish rural districts, with the exclusion of outlier data. Similarly, the Bioaccumulation Factor (BAF) of 2~~,~~796 based on observational studies on Bluegill sunfish (*Lepomis macrochirus*) (US EPA, 2009a) from PFOS contaminated freshwaters was adopted to model PFOS concentration in feral fish.

2.4 Relevance of the different foods of animal origin and tap water to PFOS intake

Theoretical occurrence data in food of animal origin and in water under the described "worst-case scenario" of locally produced food have been plotted against food consumption data, to determine intake estimates. ~~The mean Italian food consumption database~~ The mean food consumption from the Italian database(ng kg^{-1} bw d^{-1}) referred to 3–9 yr children from general population was selected as vulnerable group for a preliminary identification of the most contributing food items to PFOS exposure (Leclercq et al., 2009). Intake estimates were then compared to background levels, as those generated during the EU-granted PERFOOD project, referred to food purchased at national retailer level, mostly originating from intensive farming systems (Dellatte et al., ~~2013~~2012). As guidance value for risk characterization, the PFOS Tolerable Daily Intake (TDI) of 150 ng kg^{-1} bw d^{-1} proposed by EFSA (EFSA, 2008) was assumed: on this basis, the Margin of Safety (MOS) was calculated as ratio between the EFSA TDI and the modeled intakes: values <1 would indicate potential overexposures. The EFSA TDI is seen as absolute upper limit of "tolerable" exposure since it has been derived based on estimates from animal data having considerable faster elimination compared to humans.[1]

Food and drinking water exposure has also been found as major PFOS (and PFOA) exposure pathways for North American and European consumers due to ubiquitous and long-term uptake with modeled doses of PFOS in the range of 3 ~~to~~ –220 ng kg^{-1} d^{-1} (Trudel et al., 2008). If at contaminated sites also soils of residential areas are polluted, additionally soil intake should to be considered as a relevant exposure source for children due to mouthing behavio~~u~~r and higher soil intake (Stanek III et al., 1998).

3 Results and discussion

Based on the modeled scenario the concentrations in sewage sludges, top soils and forages are compiled in Table 2. PFOS intakes estimates (ng kg^{-1} bw d^{-1}) in the farmed species for the considered water quality-driven scenario, along with the modeled concentration (ng g^{-1}) in food of animal origin locally produced are shown in Fig. 2. These calculations are based on the compiled animal production parameters which are listed in Table 1. The resulting intakes estimates from the different modeled scenarios were calculated for Italian children 3–9 yr based on the Italian food basket (see Supplementary Material S1) are reported in Table 3. The calculations are in presence/absence (adv/no adv) of targeted advisories on local feral fish and eggs from free-range flocks consumption, and the risk characterization with respect to the PFOS TDI of 150 ng kg^{-1} bw. The comparison of intake sources in food producing animals, and finally in children in presence/absence of targeted food advisories are shown in Fig. 3.

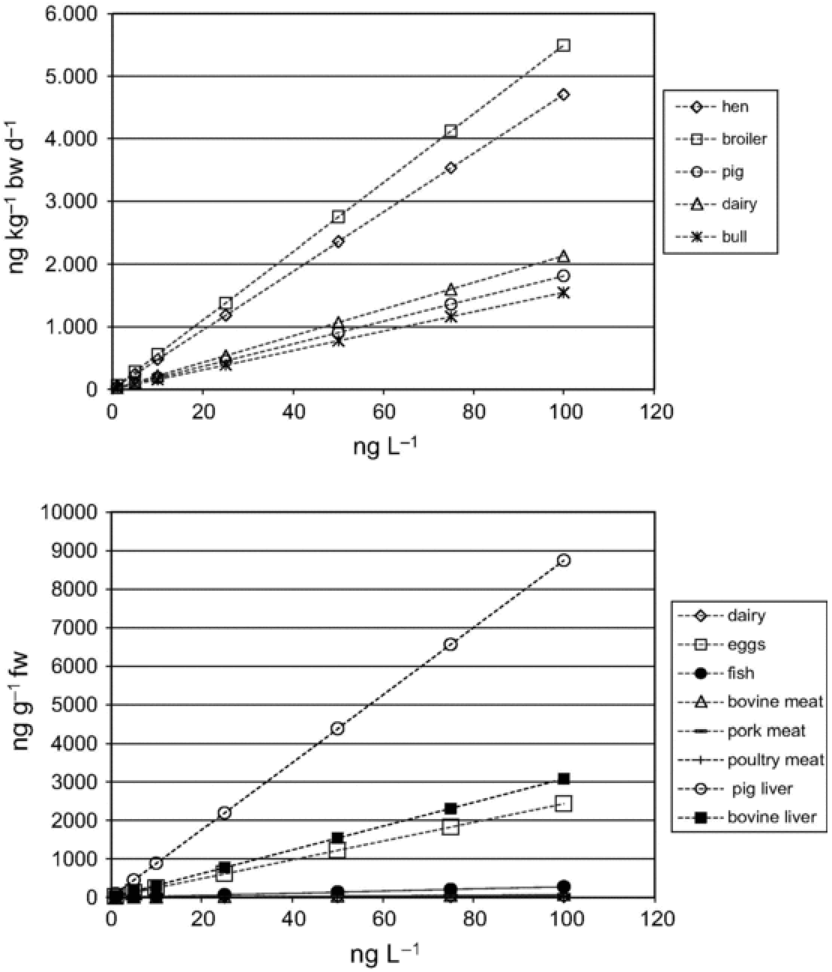

Fig. 2 Modeled intakes ng kg^{-1} bw d^{-1} of PFOS in outdoor farmed animals, above, and, below, expected concentrations ng g^{-1} fw in the related food items (*y* axis), according to the water quality scenarios (ng L^{-1}) considered (*x* axis) and their impact on agriculture top soil and forages contamination.

Table 3 Modeled food intake outcomes in 3–9 yr Italian children (ng kg^{-1} bw d^{-1}), under the water-driven case scenarios considered: comparison with the estimates on the same target from the EU PERFOOD project (Dellatte et al., 2012). Food consumption information is compiled in the Supplementary Material S1.

Scenario (ng L^{-1} PFOS in water)	PERFOOD	1	5	10	25	50	75	100
Tap water	0.01	0.01	0.04	0.08	0.19	0.38	0.58	0.77
Other beverages (bottled)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Milk and dairy products	0.16	5.46	24.4	48.1	119	237	356	474
Cheese	<0.01	0.46	2.08	4.09	10.1	20.2	30.3	40.3
Eggs	0.01	23.6	105	207	514	1025	1535	2046
Fish[a]	1.17	4.49	22.4	44.9	112	225	337	449
Beef	<0.01	0.49	2.21	4.35	10.8	21.5	32.2	42.9
Pork	<0.01	0.33	1.50	2.96	7.35	14.6	21.9	29.2
Poultry	<0.01	0.07	0.30	0.58	1.44	2.88	4.31	5.74
Offals[b]	0.01	2.01	9.10	17.9	44,5	88.8	133	177
Other fresh meat	<0.01	0.04	0.18	0.35	0.87	1.73	2.59	3.45
Cereals	0.04	0.03	0.14	0.26	0.67	1.34	2.01	2.68
Leafy vegetables	<0.01	<0.01	0.01	0.02	0.04	0.09	0.14	0.18
Root vegetables	0.04	<0.01	0.01	0.02	0.05	0.11	0.16	0.21
Other vegetables	0.01	0.01	0.03	0.05	0.12	0.25	0.37	0.49
Tomatoes	0.01	<0.01	0.02	0.03	0.08	0.16	0.24	0.32
Potatoes	0.01	0.01	0.03	0.05	0.13	0.26	0.39	0.52
Fruit	0.09	0.02	0.08	0.15	0.39	0.78	1.17	1.56
Total intake	1.57	37.7	171	337	836	1667	2499	3330
MOS	96	4.0	0.9	0.4	0.2	0.1	<0.1	<0.1
Intake with targeted advisories	na	na	42.6	84.0	208	415	622	829
MOS	na	na	3.5	1.8	0.7	0.4	0.2	0.2
Decrease %	na	na	75	75	75	75	75	75

[a] Computed on PFOS occurrence in feral species.

[b] Computed on the averaged modelled contamination in pig and bovine liver; na = not applicable.

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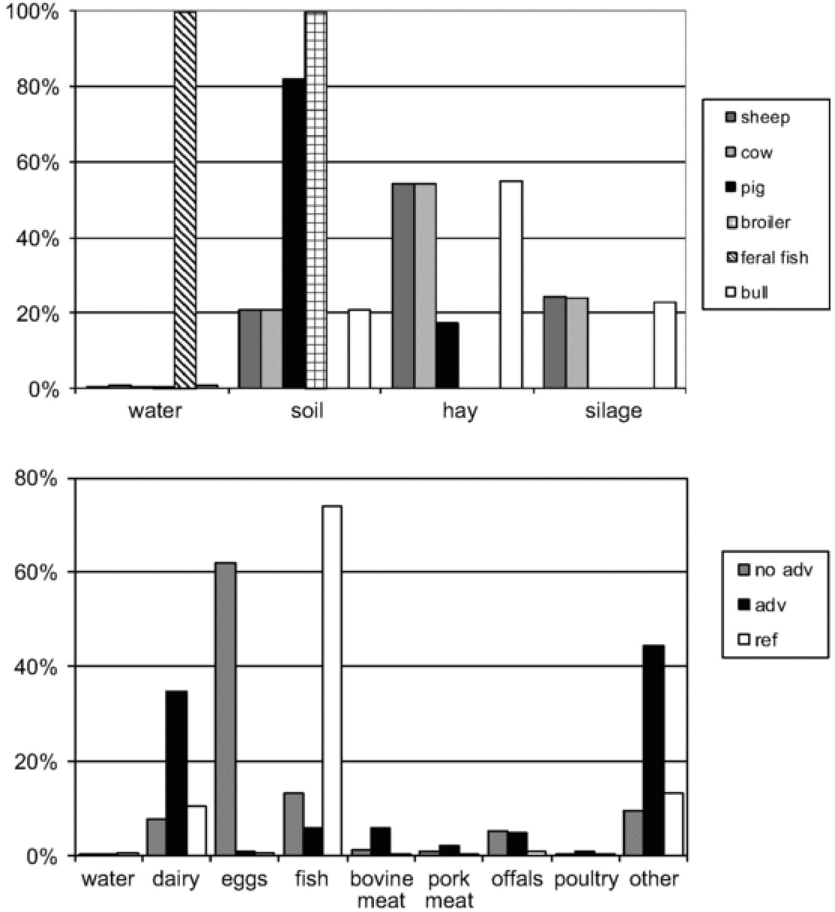

Fig. 3 Modeled average contribution from water, soil, and forages (hay and silage) as percentage on the total PFOS intake in outdoor farmed animals (above), and from main food categories in 3–9 yr Italian children (below), in presence or absence of target advisories (adv; no adv;) on fish and eggs: comparison with reference (ref) EU PERFOOD estimates (Klenow et al., 2013).

3.1 Water

The average levels of PFOS contamination in not impacted areas in drinking water samples (119 mineral waters, 26 tap water samples, 18 spring water samples) were 0.17 ng kg^{-1} bw d^{-1} for PFOS and therefore only contributed to a negligible amount to TDI (Gellrich et al., 2013).

For PFOS contaminated sites this can be different (Oliaei et al., 2013). The proposed range of PFOS contamination in water (1–100 ng L^{-1}) for this study are in line with those recently measured in surface and ground (tap) water in the North East part of Italy, under the impact of a PFAS production plant (Polesello and Valsecchi, 2013), and also in the range of European inventoried concentration in ground water (average 4 ng L^{-1}, max 135 ng L^{-1}). Also levels in European river waters (average 39 ng L^{-1}; max 1~~,~~371 ng L^{-1}) (Loos et al., 2009, 2010) and those in a Swiss river (Hus~~s~~et et al., 2009) and majority of monitored rivers in South Africa (Mudumbi et al., 2013) are within the model~~l~~ed range. In a few cases river waters such as one of the investigated rivers in South Africa (182 ng L^{-1}) have levels above the here model~~l~~ed concentrations (<100 ng). Also in case of groundwater pollution levels can be considerably above 100 ng L^{-1} around industrial landfills (Oliaei et al., 2013) or areas where firefighting foam has been used (Weber et al., 2013).

While PFOS can be removed from drinking water for human consumption by state of art drinking water treatment (Eschauzier et al., 2012; Gellrich et al., 2013), farmed animals (in particular free-range livestock) are often fed from surface water and private wells, without any filtration step which would be able to remove the contamination.

3.2 Sludges and pasture/soil contamination

The PFOS concentration in sewage sludges depends in addition on levels in waste water inflow also to some extent on the water processing cycle. Also the presence of PFOS precursor and formation of PFOS during the treatment might have an influence. However, due to the high organic carbon (OC) content (around 30% of the sludge weight on dry matter basis) and to the PFOS sorption coefficient (log K_{OC} = 3.34) (Sepulvado et al., 2011), it has been found that the PFOS sorption to the solid sludge fraction is less susceptible to the differences in water treatments of individual WWTPs compare to shorter and more polar PFAAs (Yoo et al., 2009). The modeled concentration in sludges, are in good agreement even with those recovered from low contaminated PFOS influents (Husset et al., 2009; Campo et al., 2014). Due to the anaerobic digestion of sludges for the production of bio-gas finally ending in digestates and composts as soil improver an increase up to the 40% of the former concentration in raw sludges has been observed (Yoo et al., 2009). This can most likely be explained by the degradation of PFOS precursors (Martin et al., 2010). For these sludges an adjustment factor might be used to consider this (slightly) higher level/releases from digested sludges.

The long term use of sludges or sludges-derived composts on land results in continuous PFOS input in top soil (largely in the upper 30 cm) leading to the progressive saturation of the soil binding sites in the organic carbon and clay contents (Johnson et al., 2007; Panagos et al., 2013). It is worth noting that in the EU, around the 40% of sludges from WWTPs is recycled directly or indirectly (as digestate or compost) in agriculture (Saveyn and Eder, 2014). Top soil contamination with PFOS can be also caused by inputs other than those from sludges, digestates and composts. For instance, 6 million L ha^{-1} is the yearly irrigation need for a *Zea mays* culture, in the Mediterranean area, leading to a theoretical 6 mg ha^{-1} PFOS contribution from water at 1 ng L^{-1}: the averaged application of 5.5 t ha^{-1} yr^{-1} of sludges recovered from the same water would further contribute 15 mg PFOS ha^{-1} (ARPAV, 2012). Wet depositions, with PFOS in the range of 0.1–3.3 ng L^{-1} (Dreyer et al., 2010) would result in a soil load of 1.0–33.3 mg ha^{-1} yr^{-1}, assuming an average rainfall around 1000 mm m^{-2} yr^{-1} (equivalent to 10 million L ha^{-1} yr^{-1}) in Germany and Italy, as reported by the United Nations World Statistics Yearbook. Therefore, irrigation and rainfalls may contribute to PFOS levels in soil, also in areas without inputs from contaminated sludges. Plant/crop uptake of PFOS takes place to some extent (Dreyer et al., 2010; Felizeter et al., 2012; Wen et al., 2013; Zhao et al., 2013). However, as matter of the strong PFOS binding to organic carbon and anion exchange moieties in soil texture the uptake is moderate and may e.g. lead only to a poorly efficient phyto-remediation of PFOS contamination in soils (Dreyer et al., 2010). Therefore, PFOS top soil contamination can be assumed relatively stable over time as seen by 5 yr long term study (Stahl et al., 2013). Considering the above, the modeled concentrations of PFOS in rural soils (Table 2) seem in line with that reported for the Flemish region with background levels below 0.1 ng g^{-1} dm and levels up to 38 ng g^{-1} dm in impacted areas (D'Hollander et al., 2013) and also within the range of soils from different countries (<1–483 ng g^{-1}) (Zareitalabad et al., 2013).

3.3 Soil intake

Soil intake from farmed free grazing ruminants may have some seasonal variation, as well different rates in the range 2–30% soil of the forages dm intake in ruminants, with a median of 6% considered by EFSA (2011). There is also a variation in the intake due to the timing of the harvesting of fodders such as grass for hay production: the grass cuts at the end of summer period are usually higher contaminated with soil compared to the spring cuts. Higher intakes of soils are found in those regions under drought impact or with a lower fodder yields per hectare. Here, sludge application is beneficial both for the organic carbon input and to reduce water need, but may result in a higher pollution affecting food safety and food security. For pigs and broilers, the soil intake rate at 20% and 50%, was chosen for a conservative approach, considering also the contribution from worms and insects, where PFOS concentration are expected to be higher due to bioaccumulation than those of only soil intake (D'Hollander et al., 2014).

3.4 Toxicokinetics and residues in food of animal origin

For (farmed) animals, the toxicokinetics of PFOS may vary according to the doses and the duration of the exposure. For feral fish from surface waters and free range hens, the availability of monitoring data provided a base for a bioaccumulation estimate of water-to-fish and the soil-to-egg (×2790, and ×8.9, respectively) (US EPA, 2009a; D'Hollander et al., 2011). For PFOS, such bioaccumulation is largely independent from the lipid content of the food item, in contrast to other POPs of food safety interest, such as chlorinated pesticides, polychlorobiphenyls (PCBs), and polychlorodibenzo-dioxins and -furans (PCDD/Fs). For ~~for~~ sheep in a 28-d feed trial (Kowalczyk et al., 2012), at the high dose of 1450 ng kg^{-1} bw d^{-1} higher carry-over rates have been found in liver and kidney. A similar evidence was noted in the experimental trials on broilers (Yeung et al., 2009; Yoo et al., 2009). Uncertainty arise in the above mentioned studies as well as in the studies by Numata et al. (2014) and by Lupton et al. (2014) due to low sample size, due to unclear resulting internal exposure levels and a lack of information about the degree of convergence at the steady state level. In the current modeling we considered the carry-over rates computed on the lowest experimental doses reported, because it is assumed as more in line with reported water quality, under the assumption that the PFOS in water can be transferred to the food webs via the disposal of wastewater-derived sludges on arable lands, thus leading to bioaccumulation in farmed and wild animals of alimentary interest (Figs. 1 and 2). The PFOS concentration in the target food matrices depends also on the respective animal muscle/organ burdens or on yields in the case of eggs and milk. In this respect, courtyard animals may have less weight gains than those of high inbred intensive farmed animals and therefore a longer life and exposure until they are consumed as food. Moreover, in the case of reduced yields of milk/eggs, higher contamination of PFOS in such products may be expected, because not diluted in a greater mass. For outdoor-reared pigs, the modeled concentrations in meat (0.77–46 ng g^{-1}) (Fig. 2) are in good agreement with the observational data reported in wild boars (1–29 ng g^{-1}) (*N* > 500) by Stahl et al. (2012), while those in liver seem be overestimated by a factor of ten (computed 101–8744 ng g^{-1} vs. ~~reported~~ reported <5–1780 ng g^{-1}), possibly as consequence of the large dispersion affecting the from-feed-to-liver BMF recovered from the single dose experimental trial (Numata et al., 2014).

3.5 Food exposure

To exemplify the weight of the different food items of animal origin produced locally from impacted agriculture areas on PFOS dietary intake, we considered the mean food consumption data referred to Italian children 3–9 yr diet, because in such age the amount of food eaten on kg bw basis is higher compared to adults. Furthermore, the intakes can be compared with those in the same age class within the study from the EU granted PERFOOD project activities (www.Perfood.eu). In this latter case, PFOS residue levels were analyzed in different food commodities sampled at retailer level, and in most of cases, originating from intensive farming (Dellatte et al., 2012; Klenow et al., 2013). It is generally acknowledged that intensive farmed animals have a limited contact with environmental factors, such as soil, earthworms, and in most of cases their feeding is based on large-scale produced feedingstuffs, with a reduced possibility of systematic intake of contaminated forages. Therefore, it is not surprising that also at the lowest level of

PFOS in water considered (1 ng L^{-1}), there are large differences between the intakes modeled for the contaminated area with free range animals and those estimated from the PERFOOD market basket samples (Table 2). Such large difference highlights the need of feed and food advisories for consumers and farmers~~.~~ within contaminated areas. The modeled intakes are due to the associated uncertainties not aimed for a detailed risk assessment but mainly to identify a possible prioritization for the risk management options most appropriate to reduce the exposure via food in a PFOS contaminated area. In small farms communities, living on subsistence economy, most of the food is locally produced and consumed, and the food habits may not reflect those of the general population. This vulnerable population requires targeted advisories as a pragmatic approach to reduce potential high exposures in such communities. It is worth noting in this respect that from a recent larger biomonitoring program carried out in Italy on 500 women in the reproductive age (20–40 yr old), individuals with a reported consumption of rural free range eggs showed significantly higher level of PFOS in blood than those determined in consumers of conventional eggs (Defelip et al., in preparation).

3.6 Risk characterization

As premise, in the model~~l~~ed scenario, the exposure estimates using average intake assumptions does only predict average exposure, without considering existing variation. In this study, we considered the TDI of 150 ng kg^{-1} bw proposed by EFSA (2008) based on a No Observable Adverse Effect Level (NOAEL) of 0.03 ng kg^{-1} bw d^{-1} as Point of Departure derived from subchronic studies in *Cynomolgus* (Seacat et al., 2002), with end points on thyroid hormones disruption and reduced levels of High Density Lipoproteins in plasma, by the use of an overall assessment factor of 200. From the same study, US EPA (2009a,b) derived a TDI of 80 ng kg^{-1} bw, accounting for an extrapolation factor based on the toxicokinetics differences in humans, and animals. It seems worthy to note that the above modeled TDIs might need re-assessment on the evidences of other toxicological end-points such as sperm quality (Joensen et al., 2009) or delayed pregnancy (Fei et al., 2009) having been observed in the average population being exposed to considerable lower level than the TDI and within a combined exposure assessment, also targeted on the identification of Adverse Outcome Pathways via alternative methods based on high throughput screening tests (Perkins et al., 2013).

For a risk assessment at PFOS and PFAS contaminated sites also other PFAS might need to be considered. Although PFOS has the highest or one of the highest bioaccumulation and toxicity potentials of the approx. 1000 PFAS produced today (Lindstroem et al., 2012) or formed from degradation of the produced PFAS, a range of PFAS are normally present to a varying concentration at PFOS/PFAS production sites (Weber et al., 2011; Oliaei et al., 2013). For a holistic assessment of health risk also other PFAS need to be measured and assessed for their potential adverse effects.

3.7 General discussion

For the drafted scenarios (ground/drinking water levels <100 ng L^{-1}) with contamination of soils from sludges and the consumption of locally produced food, under the presence of almost all the inventoried risk factors related to the PFOS contamination in the environment (Table 1), the tap water role in the intakes in the worst case scenario for food intake both in farmed animals and in humans is relatively low. Even under the hypothesis of the highest tap water consumption data, i.e. as those recorded during the summer season (+37 °C) in farmed animals (+40%), or accounting for the P99 of the consumption of all water-based beverages (from 7 to 70 ng kg^{-1} bw d^{-1}) in Italian children aged 3–9 yr of the general population it falls below 1% of total intake (Fig. 3). Therefore, potential risk management actions should be extended to other food items, as matter of the very bioaccumulative behavior of PFOS in the food webs (Fig. 2). The environmental quality of the water is also in this scenario still a key factor for intakes related to feral fish consumption. Feral fish is a well-known major source of PFOS intake around contaminated sites (Minnesota Health Department, 2009; Oliaei et al., 2013; US EPA, 2012). On the basis of PFOS occurrence in wild fish, the US State Authority of Minnesota and Wisconsin released the following Meal Advice as ng g^{-1} PFOS: No restrictions was suggested for PFOS levels in fish below 40 ng g^{-1}; 1 meal wk^{-1} for fishes in the of 40~~ to ~~–200 ng g^{-1}; one meal $month^{-1}$ in the range between 200 and 800 ng g^{-1} and the consumption of fish above 800 ng g^{-1} were not recommended at all (Minnesota Health Department, 2009). For the described setting such advisory is also valid and appropriate. In highly contaminated areas feral fish consumption might be advised to be completely replaced by fish with low PFOS burdens (<1 ng g^{-1} fw), in particular farmed fish fed on commercial feed (Hlouskova et al., 2013). For the inventory of management options adopted in PFOS/PFAS hot spot areas see Supplementary Materials (S2).

Of emerging interest in respect to exposure is the contribution of eggs from free-range flocks to the intake. Until now eggs have not been appropriately considered within advisories in hot spot areas. Traces of the possible role of eggs (6.89 ng g^{-1} fw as mean PFOS contamination) in determining higher PFOS intakes than those reported in other countries is present in the first Flemish assessment made by Cornelis et al., (2012), possibly reflecting the presence of a perfluorochemical plant in the outskirt of Antwerp. In general, eggs from free range hens have in average a higher level of several Persistent Organic Pollutants present in the environment due to the strong interaction of such animals with the environmental food webs and soil (Waegeneers et al., 2009). Here, the intake of soils and earthworms can also lead to a progressive biomagnifications of PFOS in a contaminated area (~~d~~D'Hollander et al., 2014). Practicable risk management options for hens/eggs may be oriented in the clustering of flocks in “clean areas” not impacted e.g. by sludge application and water irrigation. Also the feeding regime based on commercial feeds, able to minimize the pick-up of earthworms and insects from soil can be advised. Such practice has been already proposed as effective in the case of PCDD/F and of PCB presence in eggs derived from rural soil contamination (Waegeneers et al., 2009). The major practice for free range chicken on PCB~~s~~ or PCDD/PCDF contaminated areas is however the exclusion of contaminated areas or the switch to stabling.

Dairy products, even if generally lower contaminated than other food of animal origin, (Fig. 2), may be due to the high consumption volumes as relevant as fish in the overall intake (Table 3) (21 ng kg^{-1} bw d^{-1}) (see S1). This generates challenges in the release of dietary advisories, without severely affecting food security in such a rural scenario. In this respect it needs to be emphasized that the replacement of eggs from affected free range hens or change in feeding regime of the hens and stop of consumption of feral fish from contaminated areas by farmed fish or otherwise non-contaminated fish would be sufficient to reduce the daily PFOS intake by up to 75% (Table 3). With respect to the risk characterization, accounting for a 150 ng kg^{-1} bw TDI proposed by EFSA for PFOS, such replacement could be effective within a >10<25 ng L^{-1} water contamination scenario.

For other food matrices of animal origin, such as pig and bovine liver and other offal, even if reported and modeled with the highest PFOS concentrations, have a reduced overall impact on the intakes due to the low average consumption figures (0.03 g kg^{-1} bw^{-1} d^{-1} in the considered case). A specific food advisory for certain specifically affected consumer groups such as hunters and their families might be needed. Anyway, a general recommendation to limit the consumption of offal, extended also to game, such as boars, should be of some relevance in such a rural exposure scenario and accounting for local food habits, as already done e.g. in Germany (Stahl et al., 2012).

The contribution to the intake from fruit, cereals, legumes, leafy and root vegetables (24 ng kg^{-1} bw d^{-1}, see S1) have been accounted for according to the uptake factors of PFOS from soil to the edible parts (0.003 reported for corn ear, 0.1 for oat grains, 0.01 for potatoes, and 0.05 for carrots, Yoo et al., 2011; Stahl et al., 2013). Under the conservative approach of a 0.05 uptake factor extended also to fruit, the contribution of all food of vegetable origin to the overall intake represents roughly 10% of the contribution given from food of animal origin under the modeled conditions.

For individual sites, the local/national food basket needs to be used/assessed and main exposure pathways determined from there. The current compilation using the Italian food basket (Supporting Information) gives here a broad basis to be locally adjusted. For other scenarios with e.g. higher levels of PFOS in drinking water (Oliaei et al., 2013) or ground water (Weber et al., 2011) or river water (Mudumbi et al., 2013) used as drinking water source, this exposure pathway can become a more relevant source of human intake. Also if such highly polluted water has been used for irrigation of food or cattle producing areas particular concern also for food and animal products produced on these areas exist. This threat is also highlighted in the monitoring study of PFOS/PFOA levels in South African rivers (Mudumbi et al., 2013).

Overall, the development and adoption of a long-term strategy is needed in such PFOS contaminated environments. Apart from the remediation activities on the primary source of contamination, a long term strategy is needed to reduce the overall PFOS impact on the food chain and may rely on animal food safety-based parameters for the application of sludges, digestates and composts on pasture, and on field intended for fodder production, along with the implementation of good agriculture practices able to minimize the presence of soil in hay and silages.

For the overall management of such an area, information on the detailed previous use of contaminated sludges including their volume and an inventory of suspected contaminated land is needed and might require detailed monitoring. Affected areas need to be restricted for farming in particular for the access to vulnerable farmed species. Long term management plans need to be established considering the residence time of PFOS in contaminated soils and sediments. Highly contaminated soils and sediments needing remediation should be destroyed and not landfilled considering their water solubility and the recommendation from the Stockholm Convention (Stockholm Convention, 2011).

The transfer of the current worst case scenario with a large contaminated area affecting practically all food production in the area, might only be relevant to a relative small number of sites worldwide where larger volumes of contaminated sludge have been applied for a longer time. However, for many of smaller scale contaminated sites and even for firefighting foam contaminated sites, the local soil can become contaminated by ground water use over time (Weber et al., 2011) and then for the local population such as neighboring subsistence farmers in these areas a similar scenario might apply. Also, for large PFOS/PFAS contaminated megasites without larger scale industrial sludge applications on agricultural land such as in the case of 3 M site in Minnesota, certain local population doing subsistence farming around hot spots such as landfills can be particularly exposed (Oliaei et al., 2013) and need to be considered for human intake. Therefore, the basic approach of the current conceptual paper and the exposure scenarios might also be applicable for vulnerable population in industrial countries eating locally produced food while the average population in such an area consuming industrial/imported food from supermarkets might still mainly be impacted from the ubiquitous PFOS contamination of such food (Trudel et al., 2008).

3.8 Uncertainties/limitations of current modeling

The analysis of a theoretical PFOS hot spot scenario relevant for intakes includes several sources of uncertainty with respect to the knowledge base, a certain degree of subjectivity of parameter choices and model assumptions (WHO International Programme on Chemical Safety – IPCS, 2008). Although we have considered to our best knowledge the accumulation factors available for the (bio)accumulation chain of PFOS and for bioaccumulation and transfer factors in a contaminated area there are a range of uncertainties. First of all, a detailed data set from such a polluted area is missing for a validation of individual paths. While data are currently generated for such a site it will take time even for a single farm to get a comprehensive dataset. However, since the chosen factors are largely based on practical studies the order of magnitude for the individual pathways should be correct. Such assessments based on bioaccumulation factors might be for some time the only way for developing countries to assess contaminated sites they will discover when implementing now the Stockholm Convention, as there is no PFOS/PFAS monitoring capacity available.

Also, as already mentioned, for most animals bioaccumulation factors are not available, as well as appropriate information for exposure assessment such as carry-over rates.

Also the long term fate of PFOS in soil is difficult to assess. While it seems that PFOS is only slowly leached from soils (Stahl et al., 2013), parameters which might have an influence such as carbon content or pH level has not been systemically assessed.

A further uncertainty is that the total PFOS amount was used and different PFOS isomers were not considered. However, the electrochemical fluorination in PFOS synthesis leads to the production of different isomers, among which the linear form is usually predominant (70%). (Benskin et al., 2010). The non-linear PFOS isomers show different toxicokinetics in humans and animals. Non-linear PFOS isomers represent 30–55% of total PFOS in biomonitoring studies (Glynn et al., 2012), while i.e. in wild fish the 7–12%, only (Ullah et al., 2014). In most of the literature on PFOS occurrence in environmental and food matrices and also accumulation in the food chain, the total amount of PFOS is often reported and not described between linear and non-linear isomers. Since in the current study the assessment aims to predict rather the order of magnitude of contamination, such detailed considerations are not of high relevance. However, for a refining of bioaccumulation models, differences in isomer behavior might be considered. For a refined assessment also the presence of potential PFOS precursors, such as perfluoroalkane sulfonamidoacetic acids, sulfonamides, and sulfonamidoethanols in water, forages and food may lead to the formation of PFOS during the digestive array, as already noted in digestates from contaminated sludges, after anaerobic fermentation (Yoo et al., 2009). This could lead to a potential underestimation in the intakes, when analysis are targeted to PFOS only and might be considered in further assessments.

4 Conclusions

Overall, by merging the different scientific evidences coming from environmental studies and from investigation in PFOS hot spot areas, it was possible to roughly estimate the role of the different pathways and factors in determining alimentary exposures. Under a “worst case scenario” for PFOS contaminated areas with high intake of locally produced food, it seems possible to reasonably reduce the intake from local food supply chains toward~~s~~ food safety guidance levels by appropriate advisories. The implementation of such advisories might be a particular challenge for developing countries where alternative food and water supply can be challenging. Critical foods of animal origin to be targeted are eggs, wild fish and offals. Such advisories should be tailored accounting for the inventoried agriculture and animal farming practices and for the dietary habits of the local populations. Through a such empowerment about the food choices, it could be possible to make PFOS-resilient potentially exposed groups living in the contaminated hot spot, waiting for the effectiveness of environmental remediation measures adopted. Where possible, the monitoring data should be generated in particular for (potentially) exposed population. For individual contaminated sites, a site specific assessment for the individual exposure pathways is necessary, depending on the agricultural practices and the food and drinking water consumption habits. For an appropriate risk assessment and reduction of uncertainties in exposure, detailed data of PFOS and its precursors in environmental and food matrices are needed.

For validating of models the support of Duplicate Diet Studies coupled to biomonitoring investigation are likely needed but might only be available in industrial countries.[2] Such validation would also be needed to appropriately verify in the short and long-term the efficacy of risk management options adopted.

Also a detailed mapping of (potentially) contaminated areas and tailored restriction for (certain) agricultural uses are necessary. For the long-term management of such affected area the development of remediation concept are likely needed.

Considering the current epidemiological data for PFOS (Schümann, 2014), a critical assessment of the current TDI seems necessary for an appropriate risk management of PFOS exposure. Also, since normally a range of PFAS are present at contaminated sites an appropriate risk assessment need to be extended to a combined exposures to PFAS present at hot spots with the aim of an appropriate risk management to be adopted in individual hot spot areas. For such an assessment, also other PFAS should be included in monitoring and their human exposure assessed. In this respect, more research studies on toxicity, bioaccumulation, carry-over rates and exposure pathways for the other approximately 1000 PFAS are needed in addition to the gaps of PFOS exposure pathways.

5 Uncited references

European Parliament (2006), European Union, Felizeter et al. (2012), and Wilhelm et al. (2008). (Uncited references inserted in the text)

Acknowledgements

Funding to support this research was provided by the European Commission, Brussels (Belgium), Seventh Framework Project PERFOOD (PERFluorinated Organics in Our Diet) (KBBE-227525), coordinator P~~p~~rof. W.P. de Voogt~~;~~. The grant from the Italian Ministry of Health, RF 2009 No. 1534860, Project ENVI-FOOD, coordinator ~~dr~~Dr. Gianfranco Brambilla is acknowledged. Authors wish to thank Mrs. Fabiola Ferri for the tables and figures editing.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.09.050.

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Footnotes

[1] A protective TDI is rather seen at an order of magnitude lower level. This is not considered in our estimate since the derivation of a TDI is a highly complex matter and not in the scope of this study.

[2] In the case of PCB management in developing countries after 10 yrs of Stockholm Convention implementation no assessment of human exposure for critical occupations or potentially PCB contaminated sites (e.g. storage sites or transformer oil work-shops) have been made. Today in most of the developing countries also only a small amount of suspected equipment have been monitored to clarify the presence of PCB needed for an appropriate management.

Appendix A. Supplementary material

Multimedia Component 1

Supplementary data (Would you please shorten the S1 Table 1 caption as follows:) 1

Highlights

- Food of animal origin can play a pivotal role in food exposure in PFOS hot spots areas.
- Eggs from rural flocks may represent an emerging PFOS source.
- Advisories and implemented farming practice may reduce PFOS food intake by up to 75%.
- PFOS contaminated sites are problematic, due to its bioaccumulative feature.
- Level of soil contamination may represent a key factor both for food safety.

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Queries and Answers

Query: Please confirm that given name(s) and surname(s) have been identified correctly.

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