BIOMAGNIFICATION ASSESSMENT OF CONCENTRATIONS. CASE STUDY USING PERFLUOROOCTANE SULFONATE (PFOS).

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Abstract
Polyfluoralkyl compounds (PFCs) have recently received particular interest during last years due to their hazard characteristics. Unfortunately, scarce information is available for understanding their transportation, environmental fate and final sinks or loss mechanisms. This work therefore attempts to asses the relationship between PFOS levels found in biota and the trends in production volumes. For such proposal, a literature review on PFOS temporal trend was performed and the data collected was grouped by trophic categories. The results suggest different relationships between the trends in PFOS production volume and concentrations in biota from remote areas; depending mostly on the trophic status of the organisms. Factors such as the longevity of the organisms and the accumulation mechanisms of PFOS, where seasonal and reproductive conditions do not play the same role than for lipophylic POPs, could explain these finding which are essential for the long-term risk assessment . In addition, simplified models were used in this study for predicting water exposure levels from measurements in biota, resulting in estimations close to the reported measured concentration in the literature. As suggest these results, the levels found in biota can be used as a guide for understanding the fate of PFOS in the environment.

Introduction
Polyfluoralkyl compounds (PFCs) have recently received particular attention by regulatory, political and scientific community because of their persistence in the environment[1], their potential bioaccumulative behaviour[2] and their possible adverse effects on human and wildlife health[3].These amphipathic compounds, due to their lipophilic and hydrophilic qualities, have been widely used in the production of several consumer products such as commercial stain repellents, surface coatings, firefighting foams, textiles, leather, paper products, insecticides and cleaners. Among these compounds, the perfluorooctane sulfonate (PFOS) is one of the most extensively studied due to their hazard characteristics, reason by which it has been included recently in the Annex B of the Stockholm Convention.
Despite this kind of PFOS use restriction, the occurrence of this compound (and its precursors) in the environment will be being a significant trouble during next decades due to their persistence and bioaccumulation capacity and their leaching from consumer products.
Unfortunately, scarce information on sources, volumes of production, usage and emission or release to the environment is available for evaluating the repercussions of the past use of these compounds to the actual situation. In addition, the information of the actual situation (spatial and temporal distribution of PFOS and its precursors on the environment and the biota) is also limited for understanding their transportation, environmental fate and final sinks or loss mechanisms[4]
Consequently, there is a need to increase the knowledge about the environmental fate and behaviour of PFOS and its precursors and to estimate the risk due to their past and future use. Other POPs (Persistent Organic Pollutants) have showed a rapid decline in the environment after their use restriction[5]. However, PFOS has much greater affinity for the water phase than the classical POPs and that could suggest a different response to the cessation of production than has been the case of the classical POPs[6]
This work therefore attempts to asses the relationship between PFOS levels found in biota and the trends in production volumes. For such proposal, a literature review on PFOS temporal trend was performed and the data collected were analysed. In addition, simplified models are used for predicting water exposure levels from measurements in biota; checking the capacity of these models for estimating averaged waterborne exposures.

Materials and Methods

Collection and processing of PFOS data. A literature research was performed for reviewing the available information of PFOS concentration measured in biota along time. Finally, only the studies covering PFOS temporal trend in wildlife were chosen. Table 1 details the selected articles. When PFOS concentrations were not included into tables of these articles, the data were extracted directly from figures. All data collected were transferred to Excell sheet.

Three different trophic categories were established and were assigned to each specie studied in the different articles taking into consideration their diet (Table 1). Subsequently, PFOS temporal trend values were grouped by trophic categories (primary, secondary and tertiary carnivorous).

The estimation carried out by Paul and colleagues[4] of the total global PFOS-equivalents production volumes (from 1970 to 2002) were employed in this study. After 2002, the production volume was assumed to remain constant in 1300 Tn/year until 2009. This estimation of the production of PFOS-equivalents was related to PFOS bioaccumulation data.

Estimation of PFOS water concentration. The study of Martin and collaborators [16] (which reports PCF accumulation in a food web from Lake Ontario) was the base for estimating PFOS in water. Two methodologies were employed using simplified models(Figure 1A and B). In A methodology, the BSAF reported by de Vos and colleagues[17] was multiplied by the concentration measured in *Diporeia sp* from Lake Ontario. The result (estimation of PFOS food concentration) was divided by 2 assuming that the half of the *Diporeia* diet consists in diatoms[18]. The estimated concentration in these algae was multiply by BCF (reported by OECD[19]) for estimating the water concentration. In the B methodology the concentration measured in trout was multiplied by BCF.

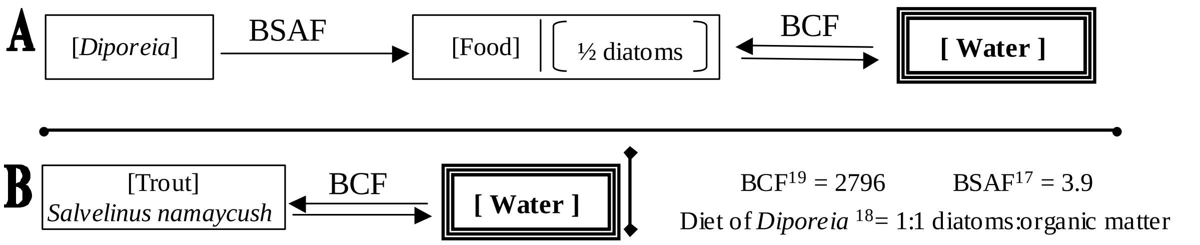


Figure1. Scheme detailing the two methodologies (A and B) employed for estimating the PFOS concentration in water. BCF: Bioconcentration Factor. BSAF: Biota-Sediment Accumulation Factor.

Results and Discussion.

PFOS temporal trend in biota and their relation to production volume. After the review of the available information published on temporal trend of PFOS in biota, only eleven studies were selected (Table 1). This scarce number of studies confirms the limited knowledge about the global presence of PFOS in wildlife to date. Figure 2 illustrates the data collected from these studies. The estimation of POFS production volumes (Perfluorooctane sulfonyl fluoride -POFS- is used to describe PFOS equivalents) along time [4] were also included in Figure 2.

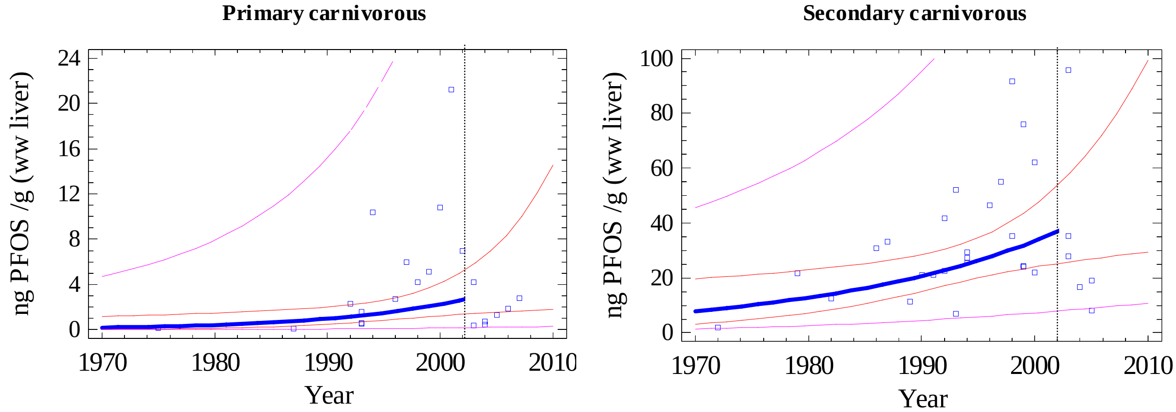
Most of selected studies found an increasing temporal trend of PFOS in biota during the years of growing production (from 1968 to 1990). During the next 10 years (from 1990 to 2000) the production remained constant in 4650 Tn/year following the study of Paul and colleagues [4] and dropped dramatically from 2002 when 3M Company (the main producer of POFS) phased-out their production. During this period, a decrease of PFOS in biota could be expected because of their metabolism. However, no clear trend could be assured for all species. Butt and colleagues[12] observed a decrease of PFOS in ringed seals as well as Ahrens and colleagues[9] in harbour seals. However, Dietz and colleagues[10] demonstrated an increase of PFOS in bears after the decline of POFS production.

In order to uniform the potential trend of PFOS relating the production of POFS, an assortment of data considering the trophic position of organisms was performed. Four of the eleven selected studies must be excluded for comparing all data together. Three of them were removed due to the reported tissue concentrations (these articles detailed eggs and whole body concentrations instead liver concentration as the rest of studies). Consequently, the comparison among data was not feasible since large differences in body burden and accumulation distribution of PFCs has been suggested[20]. The fourth eliminated study was one from Ahrens and collaborators[9]. In this work, PFOS was measured in harbour seals collected in an urbanized/industrialized area of

Germany. Thus, this study illustrates the PFOS bioaccumulation due to the PFCs release directly (release by manufacture, application and use of PFC) and indirectly (release by breakdown in the environment from POFS-equivalents to PFOS) into the environment. The rest of the studies were carried out in remote regions (excepting [15] and [16] which were excluded by differences on tissue concentrations) and consequently, the bioaccumulation corresponds exclusively to indirect release of PFCs hindering the comparison.

Figure 3 shows the temporal trend of PFOS in biota once grouped by trophic category. In the three cases (primary, secondary and tertiary carnivorous) a statistical exponential increase of the PFOS accumulation with the time could be established ($p<0.05$). The correlation found between bioaccumulation and years was improving as the trophic position increases. Indeed, the increase of PFOS in the biota can be distinguished clearly only for tertiary carnivorous (which correspond exclusively to polar bears) whereas for the lower carnivorous (primary and secondary), this increase is not so apparent. For primary carnivorous, high bioaccumulation values were not found after 2002 (phase-out of 3M production) showing a potential decrease. In the case of secondary carnivorous, one high bioaccumulation value was measured in ringed seals sampled in 2003 although a brief decrease could be also observed after 2002.

These results suggest different relationships between the trends in PFOS production volume and concentrations in biota from remote areas; depending mostly on the trophic status of the organisms. Although the uncertainty related to the limited amount of information should be considered; the data would suggest a rapid reduction in PFOS measured level in primary carnivorous, which is not reflected in tertiary carnivorous. Factors such as the longevity of the organisms and the accumulation mechanisms of PFOS, where seasonal and reproductive conditions do not play the same role than for lipophylic POPs, could explain these finding which are essential for the long-term risk assessment .



	Primary	Secondary	Tertiary
p	0.0161	0.0095	0.0000
R^2	25.65%	21.70%	68.26%
Until year	2007	2005	2006

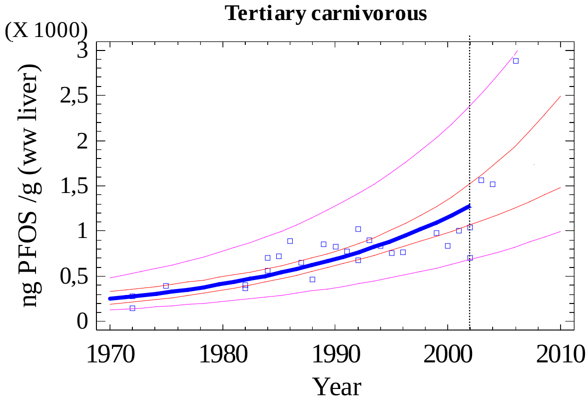


Figure 3. Temporal trend of PFOS in different species grouped by trophic categories. Bold blue lines correspond to exponential model (best fit model). The inner bounds (solid lines) show 95% confidence limits for the mean and the outer bounds (dotted lines) show 95% prediction limits for new observations.

Estimation of environmental exposure using bioaccumulation data. Measurements of PFOS in the environment are, similarly than in biota, very limited to date. However, this information can be very useful for understanding the transportation pathway of PFCs. For this reason, an extrapolation study for estimating PFOS water concentration using the accumulation data in a food web from Lake Ontario[16] was performed. Two different methodologies was employed (Figure 2 A and B) obtaining values of 60.8 pg/L and 12.8 pg/L respectively. In both cases, the estimated concentrations are in the same range of concentration found in the literature (see review of Ahrens et al. 2009[21]). As these results suggest, the levels found in biota can be used as a guide for understanding the fate of PFOS in the environment.

Acknowledgements. This work has been founded by CAM Project RESIDUOS(S-0505/AMB-0352).

References

[1] Yamashita N., Kannan K., Taniyasu S., Horii Y., Petrick G., Gamo T. *Marine Poll Bull* 2005; 51: 658.
[2] Martin J.W., Mabury S.A., Solomon K.R., Muir D.C.G. *Environ Toxicol Chem* 2003; 22: 189.
[3] Austin M.E., Kasturi B.S., Barber M., Kannan K., Mohan Kumar P.S., Mohan Kumar S.M.J. *Environ. Health Perspect* 2003; 111: 1485.
[4] Paul G., Jones K.C., Sweetman A.J. *Environ Sci Technol* 2009;43: 386
[5] Olsson M, Reutergardh L. *Ambio* 1986; 15:103.
[6] Holmström K.E., Järnberg U., Bignert A .*Enviro. Sci Technol* 2005;39: 80
[7] Hart K., Gill V.A., Kannan K.*Arch Environ Contam Toxicol*.2009; 56: 607.
[8] Smithwick M., Norstrom R.J., Mabury S.A., Solomon K., Evans T.J., Stirling I., Taylor M.K., Muir D.C. *Environ Sci Technol* 2006; 40:1139
[9] Ahrens L., Siebert U., Ebinghaus R.*Chemosphere* 2009; 76:151
[10] Dietz R., Bossi R., Rigét F.F., Sonne C., Born E.W. *Environ Sci Technol* 2008; 42:2701.
[11] Bossi R.,Riget F.F., Dietz R..*Environ Sci Technol* 2005; 39:7416
[12] Butt C.M., Muir D.C., Stirling I., Kwan M., Mabury S.A. *Environ Sci Technol* 2007a; 41:42.
[13] Kannan K., Corsolini S., Falandysz J., Oehme G., Focardi S., Giesy J.P. *Environ Sci Technol* 2002; 36: 3210.
[14] Butt C.M., Mabury S.A., Muir D.C.G., Braune B.M. *Environ Sci Technol* 2007b; 41: 3521.
[15] Furdui V.I., Helm P.A., Crozier P.W., Lucaciu C., Reiner E.I., Marvin C.H., Whittle D.M., Mabury S.A., Tomy G.T. *Environ Sci Technol* 2008; 42:4739.
[16] Martin J.W., Whittle D.M., Muir D.C., Mabury S.A. *Environ Sci Technol* 2004; 38: 5379.
[17] de Vos M.G., Huijbregts M.A., van den Heuvel-Greve M.J., Vethaak A.D., Van de Vijver K.I., Leonards P.E., van Leeuwen S.P., de Voogt P., Hendriks A.J. Chemosphere 2008; 70:1766.
[18] Landrum P.F., Nalepa T.F. *J Great Lakes Res* 1998; 24:889.
[19] OECD. ENV/JM/RD(2002)17/FINAL. 2002
[20] Ahrens L, Siebert U, Ebinghaus R. *Mar Pollut Bull* 2009; 58: 520
[21] Ahrens L., Barber J.L., Xie Z. Ebinghaus R. *Enviro. Sci Technol* 2009; 43: 3122.

Table 1. Published works used in this stuyd for assessing the temporal trend of PFOS (Perfluorooctane sulfonate) in wildlife describing the features of each study. The diet of different species was selected after traditional search information. The throphic category was assigned to each species depending on their diet.

[Ref] Reference	Specie (*Scientific name*)	Main food	Trophic category	Tissue	Period	Geographic area	Type of region
[6] Holmström et al., 2005	Guillemot *(Uria aalge)*	Migratory pelegic fish	Secondary carnivorous	Eggs	1968-2003	Baltic sea	Remote
[7] Hart et al., 2009	Sea Otter *(Enhydra lutris kenyoni)*	Bentic invertebrates	Primary carnivorous	Liver	1992-2007	Alaska costal waters	Remote
[8] Smithwick et al., 2006	Polar Bear *(Ursus maritimus)*	Ringed and bearded seals	Tertiary carnivorous	Liver	1972-2002	North America Artic	Remote
[9] Ahrens et al., 2009	Harbour Seals *(Phoca vitulina)*	Fishes	Secondary carnivorous	Liver	1999-2008	Germany	Urban / Industrial
[10] Dietz et al., 2008	Polar Bear *(Ursus maritimu)s*	Ringed and bearded seals	Tertiary carnivorous	Liver	1984-2006	East Greenland	Remote
[11] Bossi et al., 2005	Ringed Seal *(Phoca hispida)*	Polar cod	Secondary carnivorous	Liver	1982-2003	Greendland	Remote
[12] Butt et al., 2007a	Ringed Seal *(Phoca hispida)*	Polar cod	Secondary carnivorous	Liver	1972-2005	Canadian Aritic	Remote
[13] Kannan et al., 2002	Sea Eagles *(Haliaeetus albicilla)*	Fish, ducks and carrion	Secondary carnivorous	Liver	1979-2000	Germany & Poland costal	Mixture
[14] Butt et al., 2007b	Thick-billed Murres *(Uria lomvia)*	Invertebrates, some fishes	Primary carnivorous	Liver	1975-2004	Artic	Remote
	Northern Fulmars *(Fulmarus glaciales)*	Squid, jellyfish, fishes	Primary carnivorous	Liver	1975-2003	Artic	Remote
[15] Furdui et al., 2008	Lake Trout *(Salvelinus namaycush)*	Fishes	Secondary carnivorous	whole body	1979-2004	Lake Ontario	Urban / Industrial
[16] Martin et al., 2004	Lake Trout *(Salvelinus namaycush)*	Fishes	Secondary carnivorous	whole body	1980-2001	Lake Ontario	Urban / Industrial

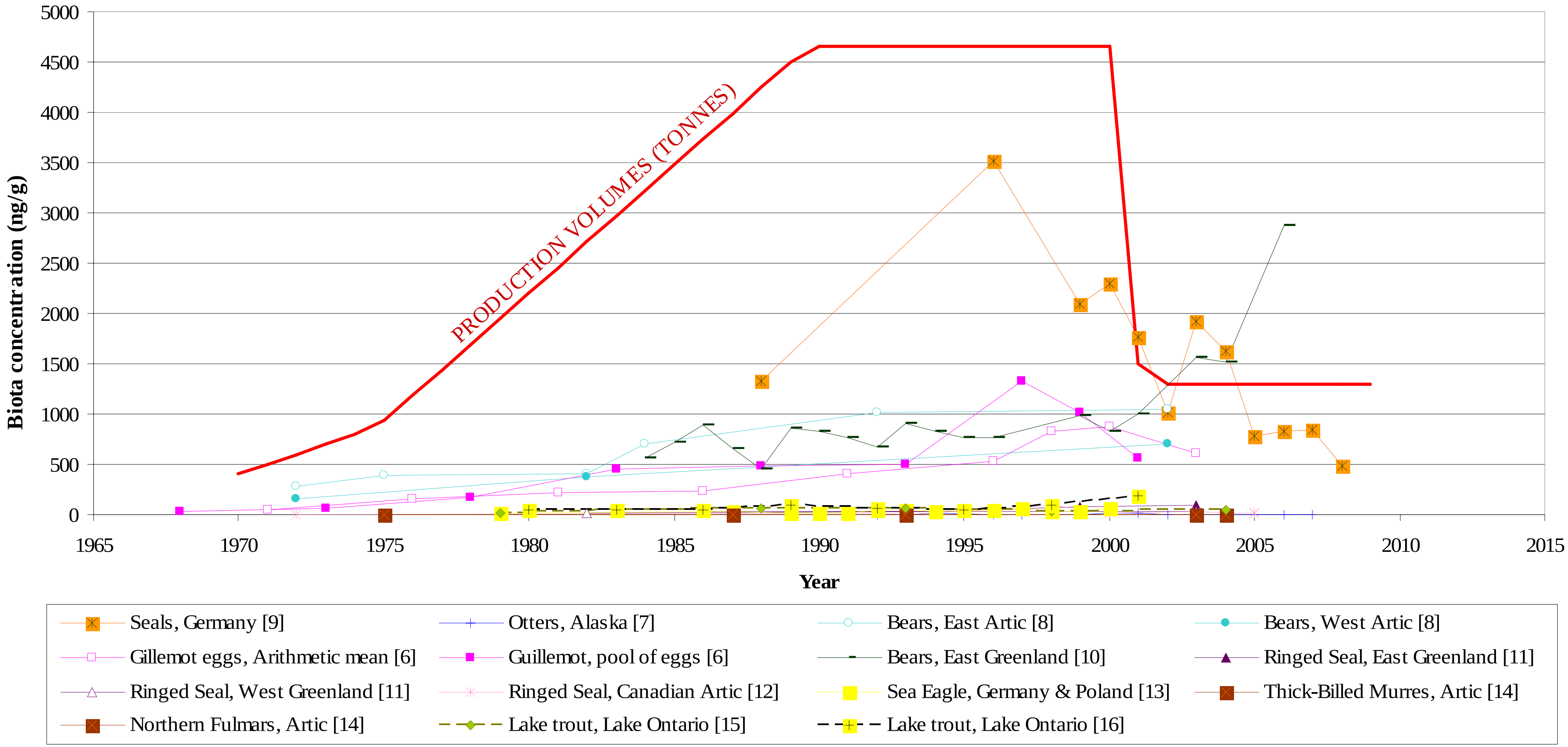


Figure 2. Temporal trend of PFOS in different species around the world (see details of studies in Table 1).