Analysis of PFCs (Perfluorinated Compounds) in California Serum: a Time Trend Study

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Introduction

Perfluorinated compounds (PFCs) used in various industrial and household products have emerged as a new class of environmental pollutants, due to their endocrine disrupting properties as well as ubiquitous and persistent distribution. We adapted/optimized an onlineaSPE-HPLC-MS/MS method based on the Centers for Disease Control (CDC) protocol. We applied this method to analyze serum samples from the 1960s, 1980s and 2000s; we investigated California PFC trend and compared with national data (NHANES).

Target Analytes and their presence

Sulfonates:

PFOS: $CF_3(CF_2)_7SO_3H$ **PFHxS**: $CF_3(CF_2)_5SO_3H$ **PFBS**:$CF_3(CF_2)_3SO_3H$

Carboxylic acids

PFOA: $CF_3(CF_2)_6CO_2H$ **PFNA**: $CF_3(CF_2)_7CO_2H$ **PFHpA**: $CF_3(CF_2)_5CO_2H$
PFDeA: $CF_3(CF_2)_8CO_2H$ **PFUA**: $CF_3(CF_2)_9CO_2H$ **PFDoA**: $CF_3(CF_2)_{10}CO_2H$

Sulfoamides

PFOSA: $CF_3(CF_2)_7SO_2NH_2$ **Me-PFOSA-AcOH**: $CF_3(CF_2)_7SO_2N(CH_3)CH_2CO_2H$
Et-PFOSA-AcOH: $CF_3(CF_2)_7SO_2N(CH_2CH_3)CH_2CO_2H$

- 12 PFCs are included in CDC's National Health and Nutrition Examination Survey (NHANES) of over 2000 participants, conducted every few years across the USA
- PFOS has been added to the list of POPs in the 2009 Stockholm Convention.

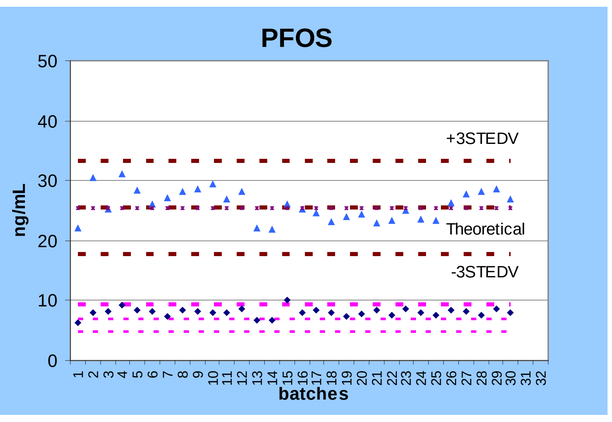
Recruitment and Sample Collection

- 1960's, (n=25): Randomly selected from archived samples from pregnant women.
- 1980's (n=30): From breast cancer Controls.
- 2009's (n=42): From a pilot study of men and women

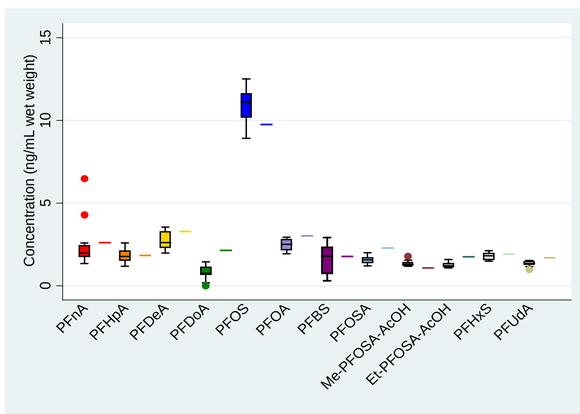
Instrumentation and Methods

- Online SPE-HPLC: Symbiosis Pharma TM from iChrom (SPE: C18 cartridge (HySphere C18 HD, 7 µm, 10 mm x 2 mm, iChrom, Plainsboro, NJ; HPLC, BETASIL C8 column (3 mm x 50 mm, 5 µm), Thermo Electro Corporation, Bellefonte, PA)
- API 4000 Qtrap (ABSciex, Foster city, CA)

Quality Control



In house QC (blank calf serum spiked with target analytes,2 levels shown here)



PFCs in QC Material from CDC values vs. experimental values

PFCs Detected in CA Serum Samples

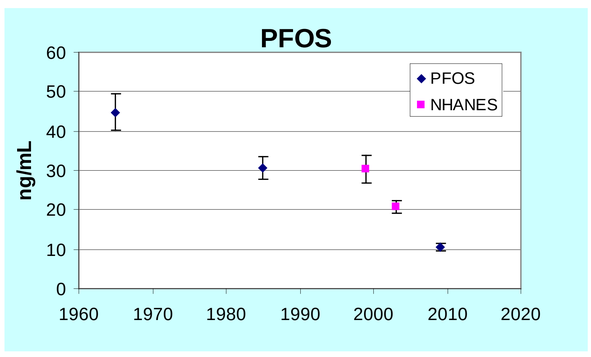
Analytes (ng/mL)	1960s (n=40) Mean	1980s (n=30) Mean	2009(n=42) Mean	NHANES (99-00) GM	NHANES (03-04) GM	LOD (ng/mL)
PFNA	<LOD	0.38	1.10	0.50	1	0.25
PFHpA	0.90	0.59	0.13	NR	<LOD	0.08
PFDeA	0.06	0.28	0.52	<LOD	<LOD	0.03
PFDoA	NA	NA	NA	NR	<LOD	0.52
PFOS	45.9	30.6	10.5	30.4	20.7	0.04
PFOA	0.30	3.17	2.63	5.20	3.9	0.07
PFBS	<LOD	<LOD	<LOD	NA	<LOD	0.24
PFOSA	0.04	0.70	0.05	0.40	<LOD	0.013
Me-PFOSA-AcOH	<LOD	0.52	0.25	1.00	<LOD	0.04
Et-PFOSA-AcOH	0.36	1.44	0.12	0.60	<LOD	0.026
PFHxS	1.77	1.77	1.02	2.10	1.9	0.008
PFUdA	0.03	0.28	0.26	NR	<LOD	0.06

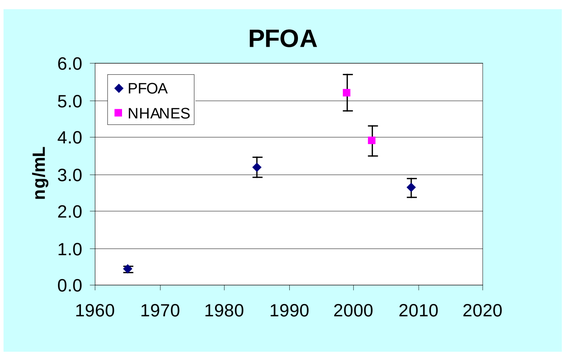
- PFOS and PFHxS were detected in all serum samples regardless of collection period.
- PFOA (95%), PFOSA (75%), and Et-PFOSA AcOH (76%), were detected in most of the serum samples Me-PFOSA AcOH were detected in most serum samples except 1960's.
- PFHpA, PFDeA and PFUdA were detected in CA 1980's serums and later, but were either not included or were lower than the LOD in NHANES data.
- PFBS and PFDoA were not detected or were lower than LOD.

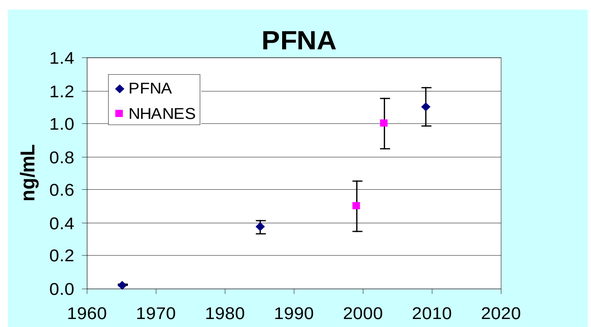
PFOS and PFOA Medians and Ranges

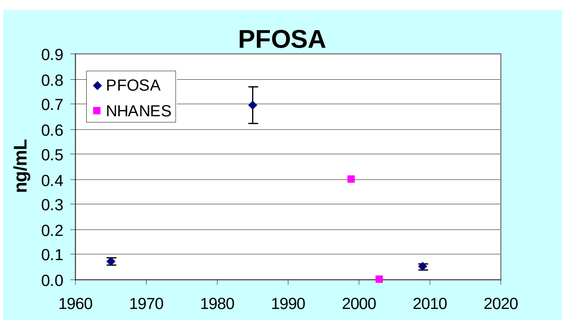
ng/mL	1960's (n=40)	1980's (n=30)	2009 (n=42)
PFOS	41.0 (8.3-124)	28.8 (13.0-69.9)	9.76 (2.66-18.2)
PFOA	0.27 (0-0.78)	2.71 (0.81-8.06)	2.08 (0.68-9.97)

Time Trend Plots of Certain PFCs









•NHANES data (1999-2000 and 2003-2004 data) were plotted as reference

- PFOA, PFHpA, PFOSA, Me-PFOSA and Et-PFOSA AcOH all showed similar trend: an increase till 1980s or up to 2000, and decrease since then.
- PFOS and PFHxS showed similar decreasing trend since 2000, which is consistent with the phase out and strict regulations, however, 1960s serum showed high presence of both.
- 1960's serum samples show unexpectedly high PFOS levels while PFOA levels are very low. This may be an artifact due to contamination during samples collection, handling and storage, or, it might indicate the presence of high PFOS in the 1960s in California. Further investigation is underway.
- PFNA, PFDeA and PFUdA showed a continuing increasing trend since the 1960s.

Conclusion and Future Work

- PFOA shows trends of increasing from 1960s to 1980s, and decreasing since 1990s/2000s.
- PFNA and other longer chain PFCAs show increasing presence in California serum since the 1960s, except for PFDoA, which has not been detected in the serum.
- PFOS, being the most abundant PFC among the target analytes, shows a decreasing trend.
- Other PFCs detected in serum samples are PFHxS, PFOSA, Me-PFOSA-AcOH, Et-PFOSA-AcOH.
- California data are well aligned with National NHANES data.

➢Further analysis of breast milk samples from California residents.
➢ More sample analysis: time trend, correlation patterns, age/gender, locations.
➢ Include more PFCs of interest: PFPeA, alcohols?
➢ Identify pathways of PFCs exposures.

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The ideas and opinions expressed herein are those of the authors and do not necessarily reflect the official position of the California Department of Toxic Substances Control.

References

NHANES data: *Environ. Health Persp.*, 2007, 115(11), 1596