A long-term trend of serum levels of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in Japanese

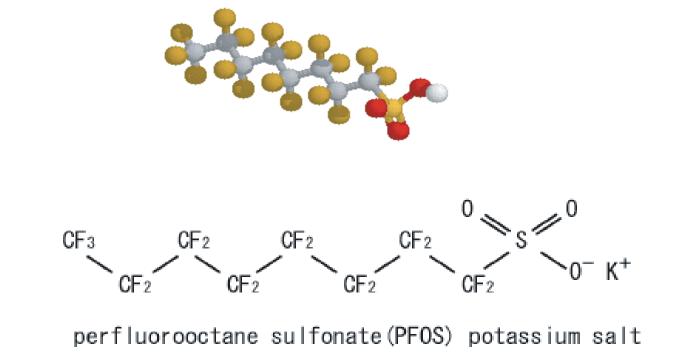
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Abstract

- PFOS and PFOA are chemicals of a new class of Pops. They have been used from 1950s as various purposes. The aim of this study is to assess a long-term trend of PFOS and PFOA exposures using serum samples collected from late 1970s to 2003 in Japan.
- Methods. We used samples in the sample bank. We collected serum samples in Miyagi (Tohoku1 samples), Akita (Tohoku2 samples) and Kyoto (Kyoto samples). In Tohoku1, Tohoku2, Kyoto, we collected samples in 1977 and 2003, in the early 1991, 1995 and 2003, in 2002 and 2003 respectively.
- Analysis: 0.5 ml of serum were used for determination of PFOA and PFOS by LC/MS. LOQ for both analytes was 0.1 ng/mL.
- Results. In Tohoku1 PFOS and PFOA concentrations have increased 3 times and 14 times, respectively. In Tohoku2, there are no increase between 1990s and 2003 for PFOS but the level of PFOA was increasing. There are large gender differences in the concentrations of PFOS and PFOA at three locations. Furthermore, there are predominant regional differences in both PFOS and PFOA concentrations. While a serum level of PFOS has reached plateau, its level of PFOA will continue to increase in next decades.

Introduction-PFOA and PFOS



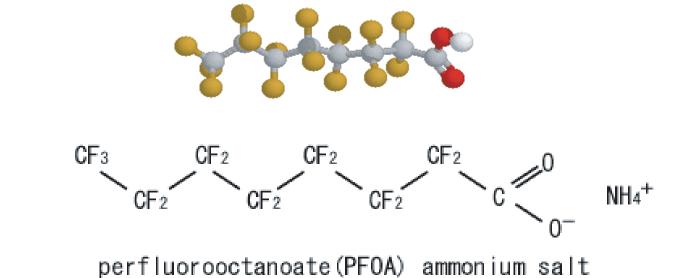
• 3M discontinued manufacturing in 2002 but other companies still

manufacture PFOA and telomers.

- PFOA may increase prostate cancer mortality in humans (Gilliland et al., 1993).
- PFOS may increase bladder cancer mortality in humans (Alexander et al., 2003)

•PFOS and PFOA are used in a variety of applications, such as in lubricants, paints, cosmetics, and fire-fighting foams.

•They are terminal products of many perfluorinated compounds and found globally in a variety of living organisms, including humans and wildlife.



Experimental design

- Serum samples : Collected about 25 years and 10 years ago, and in 2003
- Collected in Tohoku1 (the northern part of Miyagi), Tohoku2 (the middle part of Akita) and Kyoto (Figure 1).

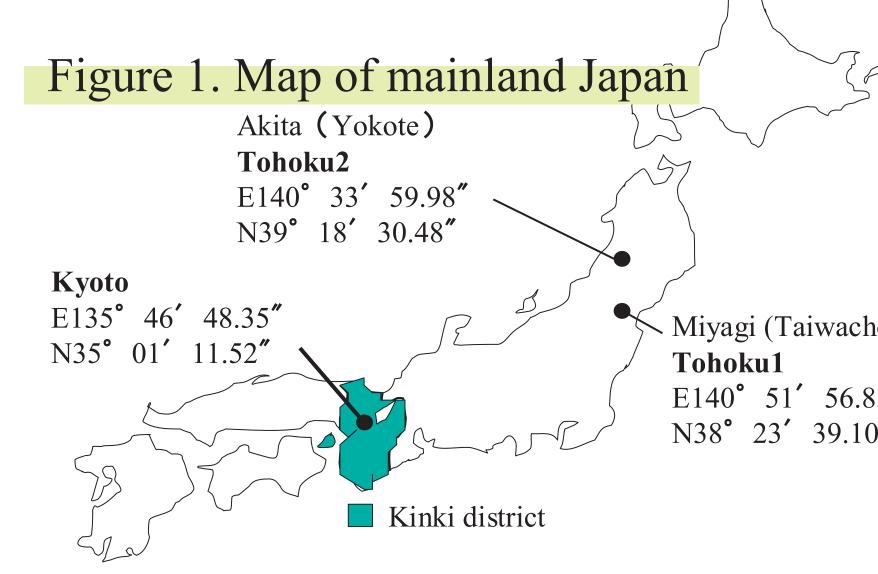


Table 1. Study population

Sampling site	Time	Male	female	Sampling site	Time	Male	female
Kyoto	2003			Tohoku2	2003		
•	No. of participants	28	26		No. of participants	66	50
	Age	36.6 <u>+</u> 11.7	37.1 <u>+</u> 10.9	(Akita)		41.3 <u>+</u> 12.5	33.5 <u>+</u> 12.2
	Residential period			, ,	Smoking		
	>=2.5y	14	20		Never	25	38
	2y-6mo	14	6		Current	38	10
	Smoking				Ex	3	2
	Never	23	25				
	Current	3	1		1995		
	Ex	2	0		No. of participants	-	40
-					Age	-	36.3 <u>+</u> 2.6
Tohoku1	2003				Smoking		
	No. of participants	32	23		Never	-	40
(Miyagi)	Age	40.3 <u>+</u> 12.2	41.6 <u>+</u> 12.5		Current	-	0
	Smoking				Ex	-	0
	Never	9	18				
	Current	23	5		1991		
	Ex	0	0		No. of participants	16	60
					Age	32.2 <u>+</u> 11.7	34.5 <u>+</u> 7.2
	1977				Smoking		
	No. of participants	-	39		Never	3	60
	Age	-	47.2 <u>+</u> 6.4		Current	13	0
	Smoking				Ex	0	0
	Never	-	39				
	Current	-	0				
	Ex	-	0				

Extraction & analysis

- Ion pair extraction (Hansen et al. 2001)
- LC/MS (Saito et al. 2004)
- LOQ: 0.1 micro g/L for PFOA and PFOS

Table 2 .Geographic differnces in serum concentration of PFOS and PFOA in 2003

		Male				F	Sex difference				
Sampling site	No.	GM	GSD .	ANOVA	No.	GM	GSD	ANOVA	t-test		
	PFOS (μg/L)										
Kyoto	14	28.1	1.5	A	20	13.8	1.5	A	< 0.01		
Tohoku2	66	12.9	1.5	В	50	6.9	1.4	В	< 0.01		
Tohoku1	32	5.7	1.8	C	23	3.5	2.9	C	< 0.05		
				PF	OA (µg/	L)					
Kyoto	14	12.4	1.4	A	20	7.1	1.4	A	< 0.01		
Tohoku2	66	3.4	1.5	В	50	2.5	1.6	В	< 0.01		
Tohoku1	32	3.3	2.0	В	23	2.8	1.5	В			
ANIOTIA D'C	$C = \sqrt{1}$	· 1·	1 11 1 11 1		1'	1	' ' ' 11 1	'CC / (D <0			

ANOVA: Different letters indicate that their corresponding values are statistically different (P<0.001). t-test: student's t-tset between Male and Female No.:Number of participants; GM: Geometric Mean; GSD: Geometric Standard Deviation

The geometric means of serum PFOS and PFOA concentrations were higher in males than females for all samples collected in 2003 Age class and smoking status did not influence the PFOA or PFOS serum levels

Table 3.PFOS and PFOA levels in sera in Kyoto samples

	M	ale		Female				
Origin	Kyoto a)	Other b)	p value c)	Kyoto a)	Other b)	p value c)		
No. of participants	14	14		20	6			
PFOS (μg/L)								
GM	28.1	21.8	< 0.01	13.8	9.4	0.053		
GSD	1.5	1.7		1.5	1.3			
PFOA (μg/L)								
GM	12.4	7.1	< 0.01	7.1	3.7	< 0.01		
GSD	1.4	1.4		1.5	1.3			

a) Lived in the Kyoto area for at least 2.5 years
b) Had moved into the Kyoto area within the previous 6 months to 2 years
c) student's t-test between Kyoto and Other

Table 4. Long-term exposure trend of

serum PFOS and PFOA

		Male						Female					
		PFOS	(μg/L)	PFOA	(μg/L)		PFOS	(μg/L)	PFOA	(μg/L)			
Sampling site	Date	GM	GSD	GM	GSD	No.	GM	GSD	GM	GSD	No.		
Tohoku1	2003	5.7	2.0	3.3	2.0	32	3.5	2.9	2.8	1.5	23		
(Miyagi)	1977	-	-	-	-	-	1.1	1.8	0.2	2.0	39		
	p value	2 -		_			< 0.001		< 0.001				
Tohoku2	2003	12.9	1.5	3.4	1.5	66	6.9 ^A	1.4	2.5 ^A	1.6	50		
(Akita)	1995	-	-	-	-	-	8.7^{B}	1.3	1.9 ^B	1.4	40		
	1991	10.2	1.5	2.2	1.4	16	7.9 ^A	1.4	1.8 ^B	1.5	60		
	p value	2		< 0.001			< 0.05		<0.05#				

Discussion

- Geographic differences in serum levels are in agreement with environmental PFOS and PFOA contamination
- There is an intensive PFOA source in Osaka close-by Kyoto (Saito et al., 2004)
- PFOS and PFOA levels of tap water in Kyoto area are higher than Tohoku area.
- The increasing trend in serum levels of PFOA may be correlated with trend in industrial activities in Japan

Conclusion

- Human exposure to both PFOS and PFOA was more intensive in Kyoto than in the other areas
- Serum levels in Kyoto samples were close to those in the US (Hansen et al. 2001)
- Sex and residential area are the most influential factors, while age and smoking status are not so influential
- Serum concentrations in Tohoku1 samples increased by a factor of 3 for PFOS, and a factor of 14 for PFOA
- PFOS levels have reached a plateau in the mid 1990s, but PFOA concentrations have been steadily increasing since 1977

References

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