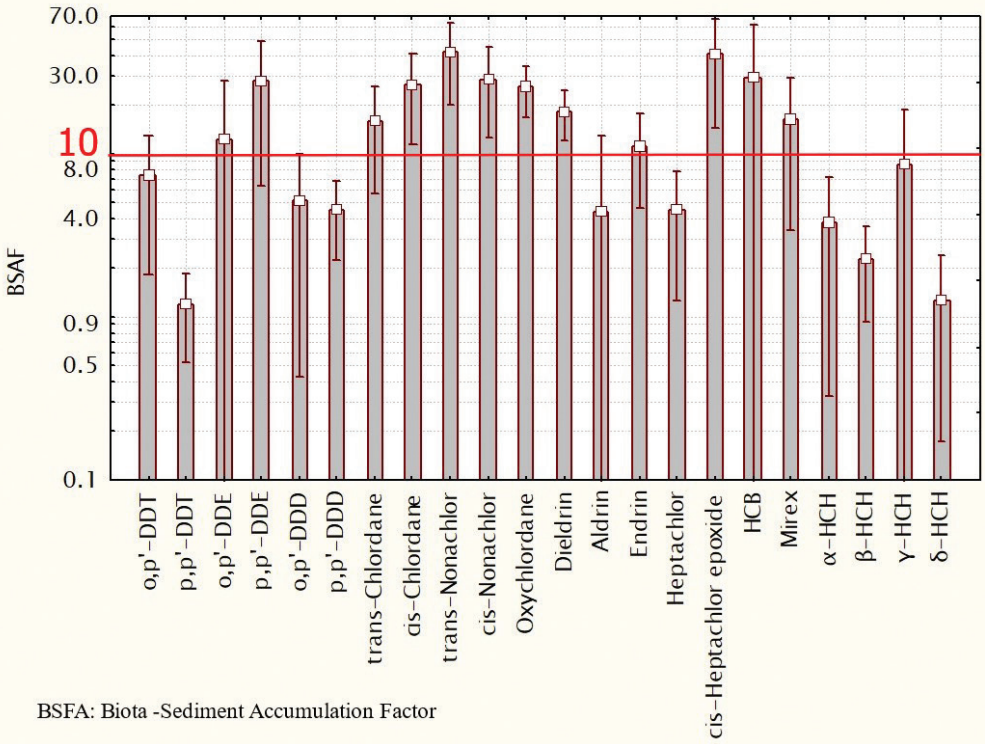
BSAF Values of Pesticides for Crucian Carp



BSFA: Biota -Sediment Accumulation Factor

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Sex Difference in Concentrations and Maternal transfer During the Spawning Season

Compound	Male	Female	Egg	Transfer ratio, %
Dioxins	1.2	1	0.59	21
DDTs	1.7	1	0.60	25
Chlordanes	1.4	1	0.54	23
Drins	1.6	1	0.95	34
Heptachlors	1.5	1	0.74	28
HCB	1.2	1	0.77	30
Mirex	1.4	1	0.64	26
HCHs	1.5	1	0.60	26
PBDEs	1.4	1	0.51	21

DDT; p,p'- & o,p'-DDT, p,p'- & o,p'-DDE, p,p'- & o,p'-DDD; Chlordanes: trans- & cis-chlordane, trans- & cis-nonachlor, oxychlordane; Drins: aldrin, endrin, dieldrin; Heptachlor: heptachlor, trans- & cis-heptachlor epoxide; HCHs: α-, β-, γ- & δ-HCH

32

II-4 <2007~2008>

Environmental monitoring and risk assessment of perfluorinated compounds

Japan – Norihisa TATARAZAKO, Norimitsu SAITO, Kazuaki SASAKI
Korea – Hyunmi KIM, Hyeonseo CHO

1. Background

Perfluorinated chemicals like PFOS and PFOA are persistent in the environment and have been shown to bioconcentrate in aqua-organism. It has been detected in a number of species of wildlife, including marine mammals. Its persistence, presence in the environment and bioaccumulation potential indicate cause for concern. It appears to be of low to moderate toxicity to aquatic organisms but there is evidence of high acute toxicity to honey bees. Perfluorinated chemicals have been detected in sediment downstream of a production site and in effluents and sludge from sewage treatment plants. Given the apparent widespread occurrence of perfluorinated chemicals, national or regional exposure information gathering from soil, water, sediment, biota (blood and liver of fish etc.) and risk assessment may need to be considered. Korea and Japan cooperate to monitor the amounts of perfluorinated chemicals from several media and living materials in both countries. Several toxicity experiments will be performed. With monitoring results from both countries and relevant toxicity data, the risk assessment of the perflourinated chemicals will be performed.

2. Research Plan

The research cooperation between Japan and Korea on the “Comparison of monitoring data for Perfluorinated chemicals” includes the followings:

1) Regional monitoring of perfluorinated chemicals
2) Biological accumulated data from bio-organisms
3) Production of toxicity data using aqua-organisms

3. Major Outcomes

For PFDA (C10), PFUnDA (C11), and PFDoDA (C12) analysis, PFCs adsorbed in sample pre-treatment apparatus (bottles, filtration system) is quite significant, so they should be recovered by rinsing with Methanol. In order to get precise chromatograms of PFCs in water samples, it is necessary to keep enough retention time. Composition ratio of PFCs in the stream water was as follows; PFNA (C9) > PFOA (8) > PFOS (8)> PFDA(C10)> PFUnDA (C11)

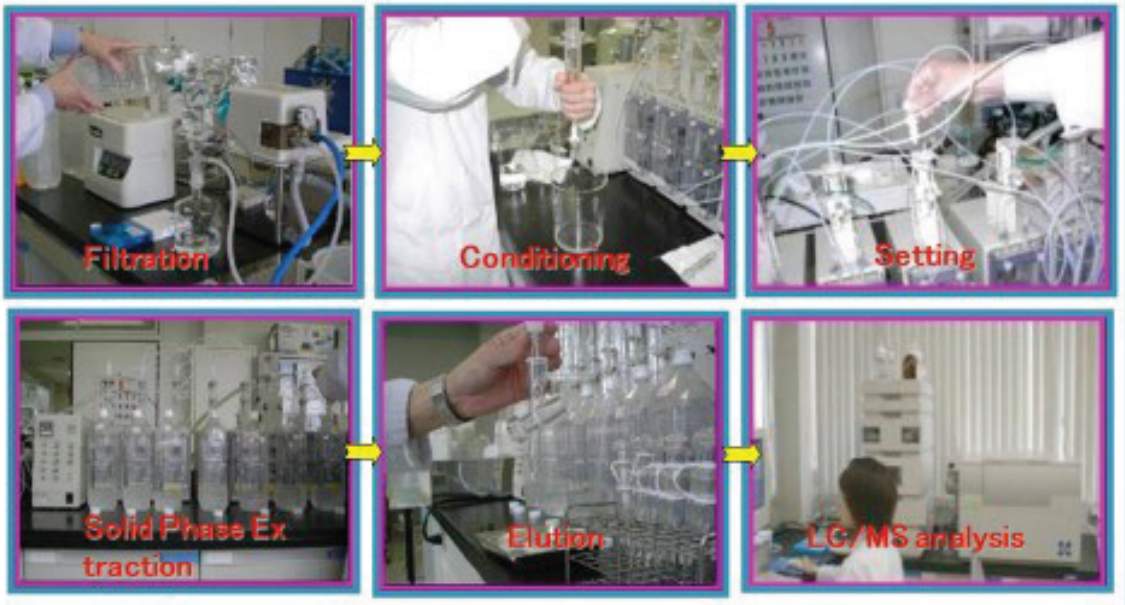
Analytical conditions of LC/MS/MS

a) HPLC	
Instrument	Agilent 1200 Series
Analytical column	ZORBAX Eclipse Plus C18 (2.1mm × 100mm, 1.8 μm)
Column temp.	40 ℃
Mobile phase	A: 10 mM CH_3COONH_4/H_2O
	B: CH_3CN (LC/MS grade)
Injection volume	10.0 μL

b) LC/MS/MS	
Instrument	Agilent 6410
Ionization	ESI (Negative mode), MRM
Prec. Ion	M-1
Prod. ion	M-45 (Perfluorocarboxylic acids)
	80, 99 (Perfluorosulfonic acids)
Frag. Voltage(v)	50-100 (Perfluorocarboxylic acids)
	150-200 (Perfluorosulfonic acids)
CE(v)	5 (Perfluorocarboxylic acids)
	55 (Perfluorosulfonic acids)
Drying gas	N_2 (5 L/min, 300 ℃)
Vapor Temp.	150 ℃
Nebulizer	N_2 (60 psi)
Capillary	2000 v
Delta EMV	400 v

c) Gradient

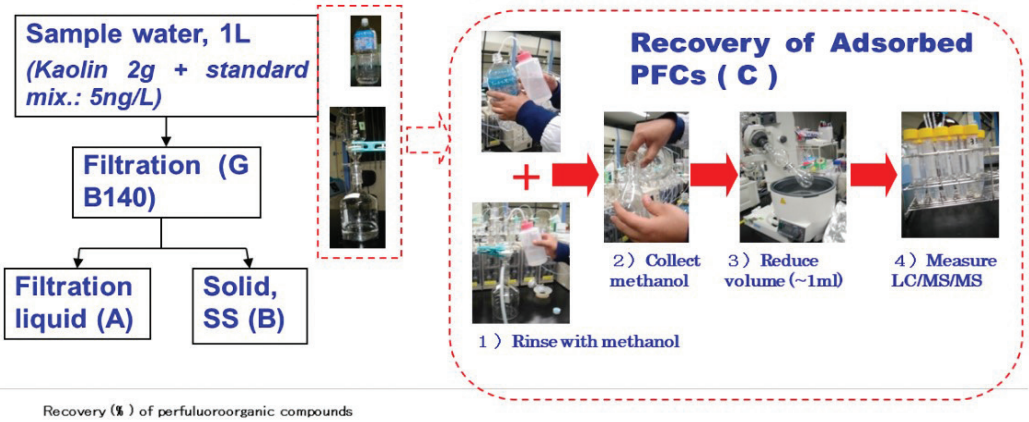
Time [min]	Flow rate [mL/min]	Solv. A [%]
0	0.2	70
4	0.2	70
20	0.2	25
25	0.2	25
26	0.3	10
34	0.3	10
35	0.2	70
45	0.2	70



Water Sample preparations for PFCs analysis

This figure shows steps of the preparation processes for surface water. Two liters of surface water samples were first filtered through both a glass fiber filter to remove sediments. Water concentrator system was equipped with Presep-C Agri cartridge column for solid phase extraction, through which 1L of the sample water were passed. The cartridge column was then eluted with 2 mL of methanol. Finally, it was concentrated at room temperature under nitrogen gas flow to 1 mL for LC/MS analysis.

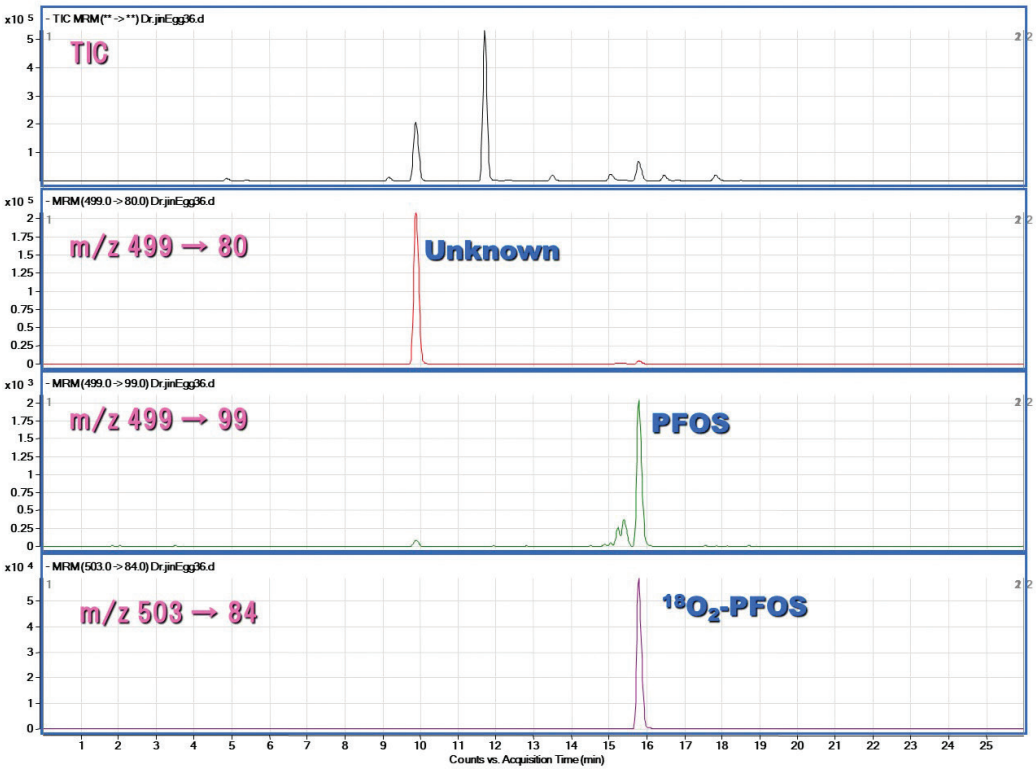
Behavior of PFCs separated through filter paper (GB140; 0.4μm)



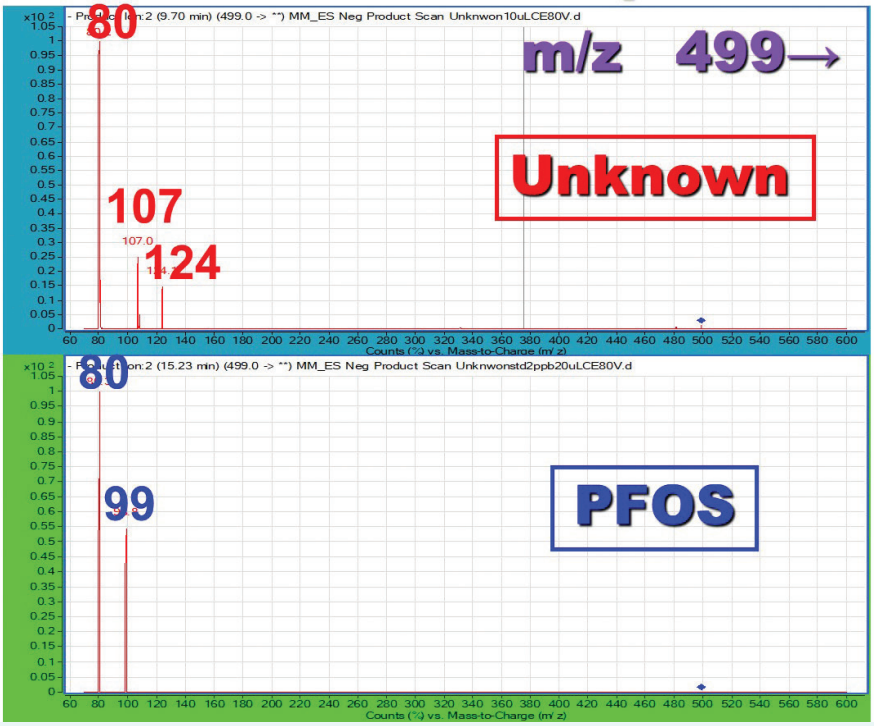
Recovery (%) of perfuluoroorganic compounds

	Carboxylate								Sulfonate			
	PFPeA (C5) [MS:263]	PFHxA (C6) [MS: 313]	PFHpA (C7) [MS: 363]	PFOA (C8) [MS: 413]	PFNA (C9) [MS: 463]	PFDA (C10) [MS: 513]	PFUnDA (C11) [MS: 563]	PFDoDA (C12) [MS: 613]	PFBuS (C4) [MS: 299]	PFHxS (C6) [MS: 399]	PFOS (C8) [MS: 499]	PFDS (C10) [MS: 599]
A (%)	11.6	58.6	94.9	102.9	104.5	85.6	40.1	17.9	56.6	108.1	97.7	31.0
B (%)	0	0	0	0	0	0.01	0	0.07	0	0	0	0.0536
C (%)	0.3	0.1	0.1	0.5	1.5	12.3	44.1	74.7	0.0	0.0	6.3	64.0
Total (%)	11.9	58.7	95.0	103.4	106.0	97.9	84.2	92.7	56.6	108.1	103.9	95.1

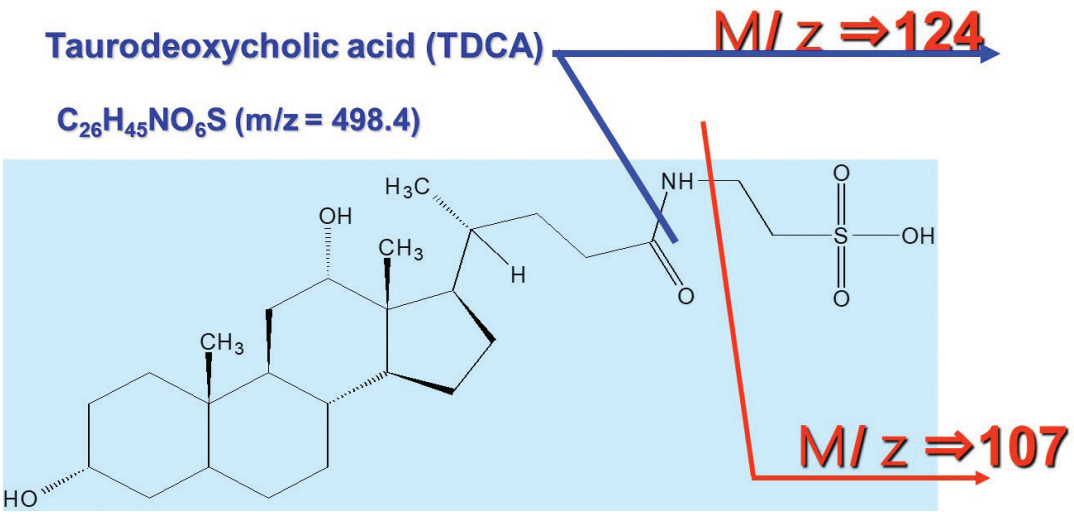
Chromatograms of PFOS in animal sample



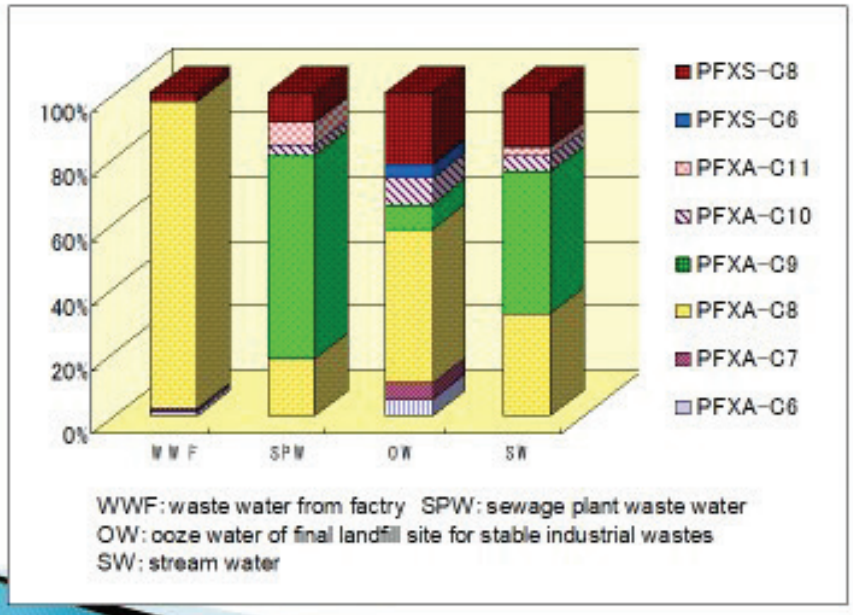
Comparison of product ion between PFOS and unknown compound



What is the unknown compound ?

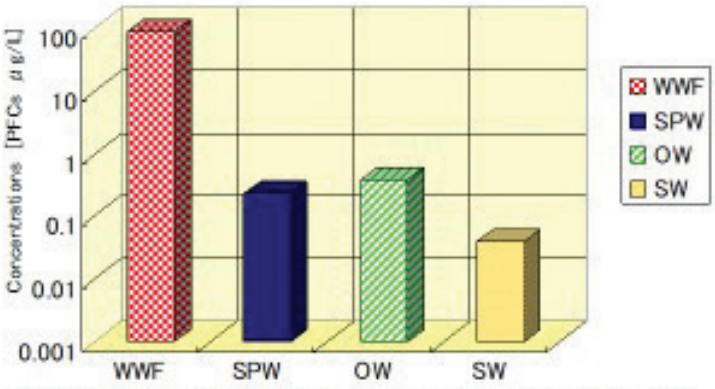


Composition ratio of PFCs



WWF: waste water from factry SPW: sewage plant waste water
OW: ooze water of final landfill site for stable industrial wastes
SW: stream water

Concentration of PFCs



WWF: waste water from factry SPW: sewage plant waste water
OW: ooze water of final landfill site for stable industrial wastes
SW: stream water

III–1 <2009~2011>

Harmonization of Analytical Methods for Dioxins and POPs/new POPs between Japan and Korea

Japan – Yasuyuki SHIBATA, Yoshikatsu TAKAZAWA
Korea – Samcwan KIM, Jongwoo CHOI

1. Background

The Article 16 of the Stockholm Convention asked the Parties to conduct environmental monitoring on priority media, including air, and submit "comparable" monitoring data to the Convention as an effort for the reduction of the global contamination by POPs, such as dioxins, PCB and organochlorine pesticides. As a joint research theme in this Korea-Japan bilateral program, harmonized POPs air monitoring method has been developed and was used in both countries to obtain POPs data in remote areas, which were reported in the first Regional Report of the Effectiveness Evaluation of the Stockholm Convention in Asia-Pacific.

Meanwhile, additional 11 candidate chemicals for the Convention have been submitted, among which 9 chemicals, i.e., pentabromodiphenyl ether, octabromodiphenyl ether, hexabromobiphenyl, chlordecone, PFOS, α-HCH, β-HCH, γ-HCH, and pentachlorobenzene, were concluded to be added to the Convention by the POPs Review Committee. It is necessary for the Parties, therefore, to establish monitoring method for the additional candidates and other related chemicals together with the original 12 POPs in order to conduct environmental monitoring and report data for the next effectiveness evaluation.

For corresponding to the necessities mentioned above and devoting to the prevention of global-scale POPs and related chemicals contamination, both Japan and Korea will continue development of the precise and accurate monitoring methods, including development of both sampling system and analytical instrumentation as well as QA/QC protocol, in order to conduct monitoring in both countries as well as to play a key role together for the research developments of other Asian countries in the field of regional/global POPs monitoring.

2. Research Plan

1) Develop air monitoring method of new POPs together with original POPs, particularly in background area.

2) Develop and apply new technique, such as GC/MSMS, for the monitoring.

3) Harmonize with the detailed QA/QC procedures on POPs sampling and analysis method.

4) Develop automatic sampling system of several samples in remote islands (by Japan)

5) Develop sampling equipment to address Aldrin recovery problems in POPs monitoring (by Korea)

6) Compile information on new POPs sampling and analytical methods in the air with QA/QC procedures for harmonizing methods in both countries

7) Develop analytical methods of stable isotopes ratio for tracing POPs in environmental forensic science

3. Major Outcomes

<KOREA>

1) In the existing POPs monitoring results, the recovery rate of some Aldrin is presented as 80~101%, 69~85%, etc., while others present the recovery rate of Dieldrin or the sum of Drins rather than the direct recovery rate of Aldrin.

2) During the POPs monitoring process in background air in Korea, the recovery rate of Aldrin was very low at 7-9%, so in this study, the influence of aspiration speed, chemical decomposition, surrogate spiking media(ACF), and additional impinger system on the recovery rate of Aldrin during the sampling process were investigated. A study was conducted to find clues to the low recovery rate of Aldrin.

3) In the newly manufactured impinger system (QFF + PUF + ACF + Diethylene Glycol in Impinger), Aldrin showed a good recovery rate of 60.5 to 75.5% indoors, but a very low recovery rate of 0.1 to 14.9% outdoors.

4) Research results of aldrin in the ambient air include (1) short half-life (minimum 0.9 hours), (2) outdoor recovery rate of less than 10%, (3) indoor recovery rate of more than 70%, (4) ozone treatment indoor recovery rate of less than 10%, and (5 no metabolites detected during sample collection. Based on this, when aldrin is exposed to the ambient air, it reacts with ozone and is oxidized to dieldrin in a short period of time, and the unstable dieldrin is again converted into alcohol, ketone, and acid very quickly. The metabolic pathway in progress was proposed.

<JAPAN>

1) A commercial high volume sampler was found to contain Teflon and Teflon-coated metal parts which show detectable levels of PFNA (perfluorononanoic acid).

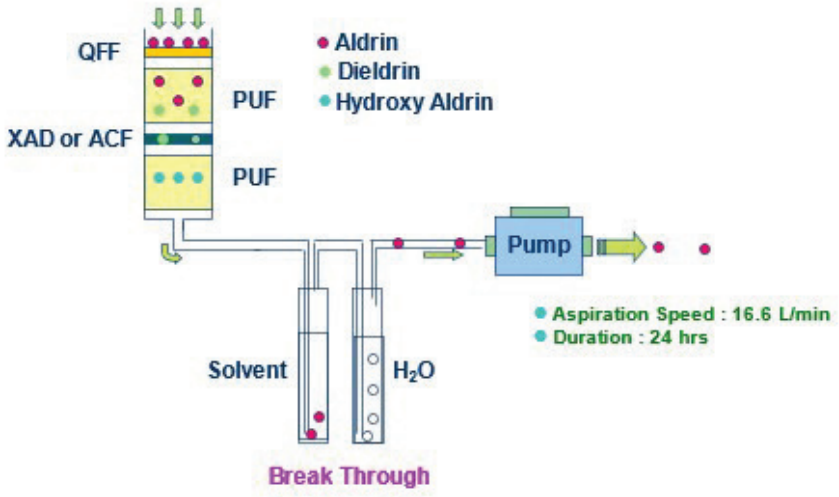
2) Anti-vibration sheet used in a commercial HV sampler was found to be contaminated by some POPs/new POPs chemicals. Detected contaminants in the sheet included PCB, HCB and other chlorobenzenes, PCN, and HCHs.

3) A new, automated air sampler for POPs/new POPs chemicals with thermal desorption technique showed the possibility of POPs collection with satisfactory recovery. The sampler is planned to use with another newly developing instrument, TD-GCxGC/MSMS, which is highly sensitive with quite wide dynamic range and high selectivity.

4) POPs monitoring at a remote island, Hateruma, with a high volume sampler has been continued once a month in FY 2010. Like in the previous data, HCB was a dominant chemical among POPs pesticides in c.a. 100 pg/m^3 levels. No particular “event” could be detected during the period. HCB showed a moderate increase in Spring season (April ~ June) than other seasons.

Japan-Korea Bilateral program meeting (8 Mar. 2010)

❖ Breakthrough Test

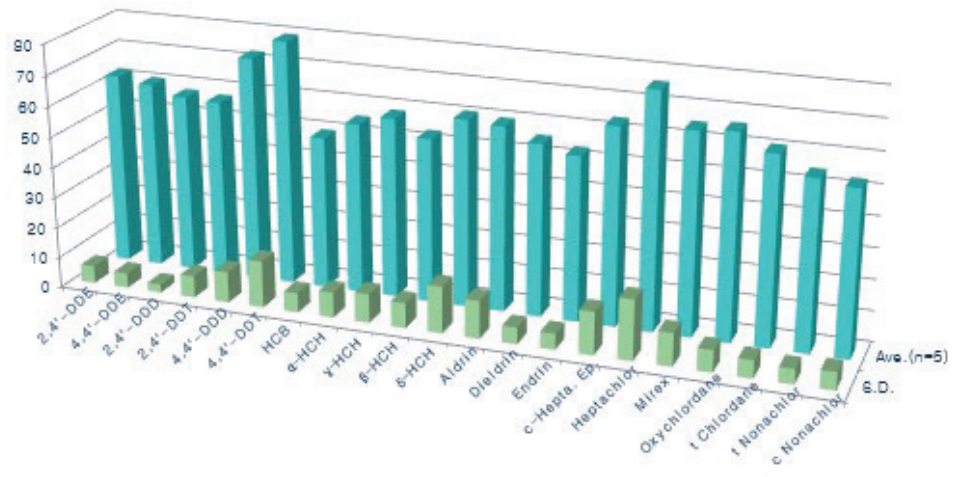


Lab. Scale Experiment Apparatus

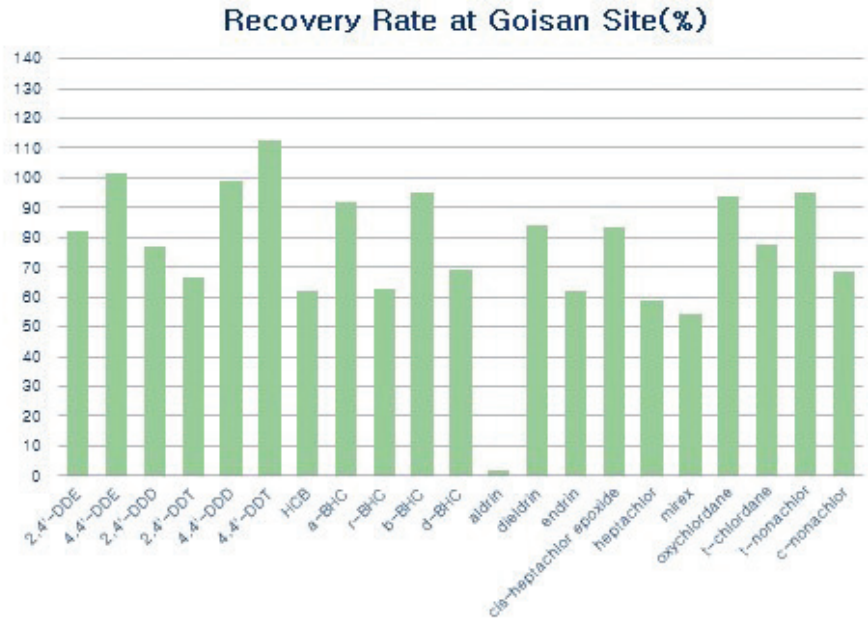
30

Korea-Japan Bilateral program meeting (15 Feb. 2011)

❖ Recovery Rates of Surrogates treated on QFF with the Impinger Type Air Sampler at Indoor Condition

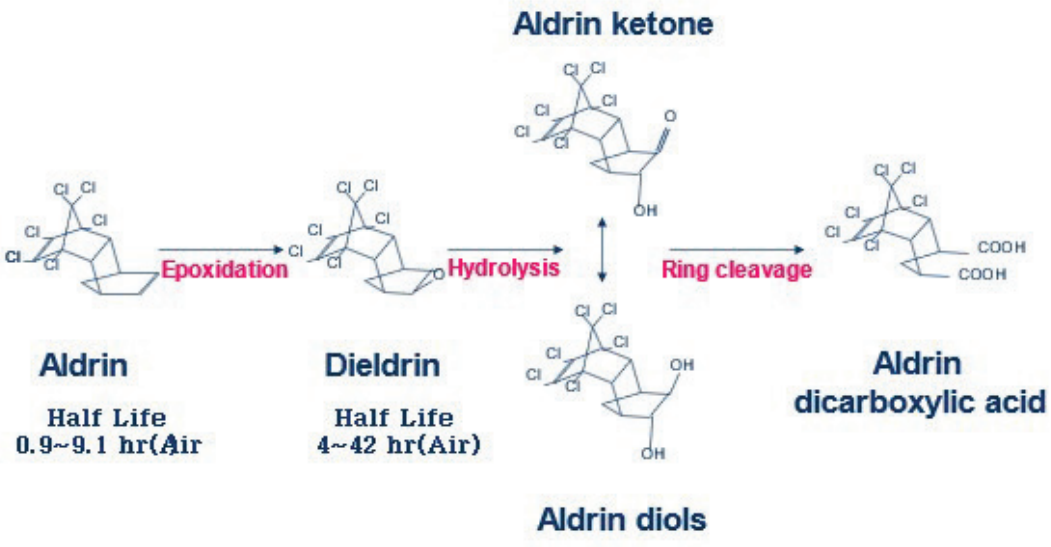


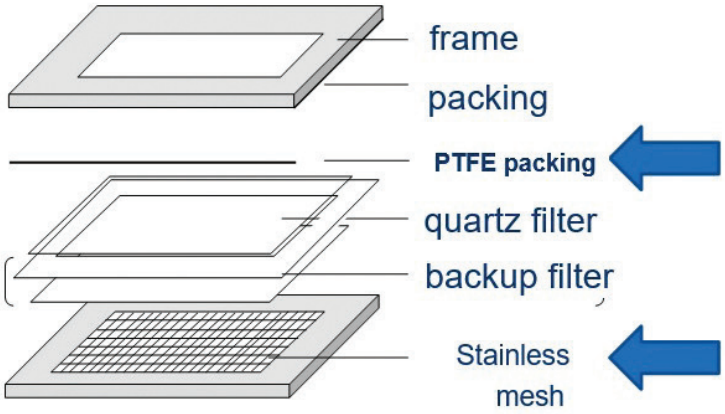
❖ Recovery Rates of Surrogates treated on QFF with the Impinger Type Air Sampler at Goisan Site



Korea-Japan Bilateral program meeting (15 Feb. 2011)

❖ Metabolic Pathway of Aldrin (guessed)

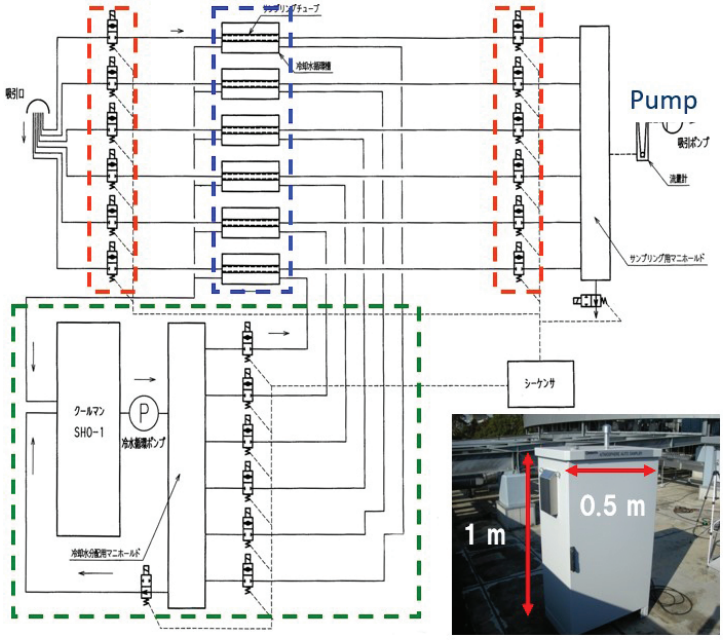




PFOA, PFNA

Use of "Teflon" plate and coating for HV sampler

Outline of automatic POPs air sampler based on thermal desorption technique



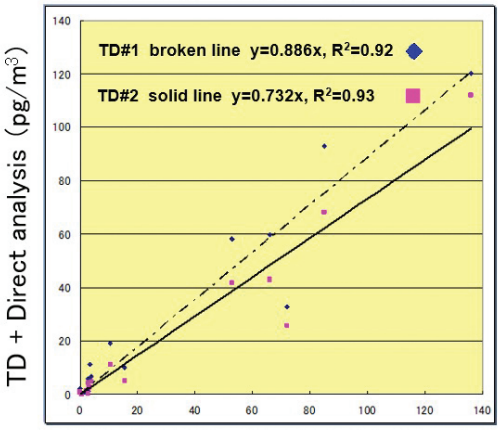
Time Resolution:
1sec ～ 100hrs

Vacuum Speed:
0.01 ～0.5L/min

Tenax TA Tube:
length 60mm, i.d. 4mm

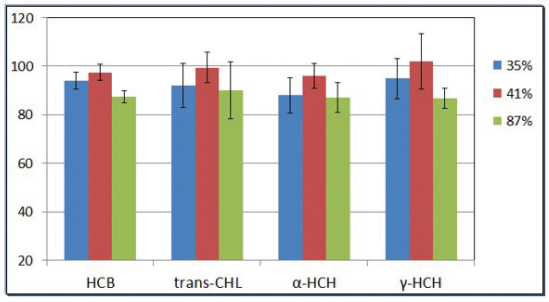
Continuous Samplimg:
6 ～12 samples

Comparison of HV and TD



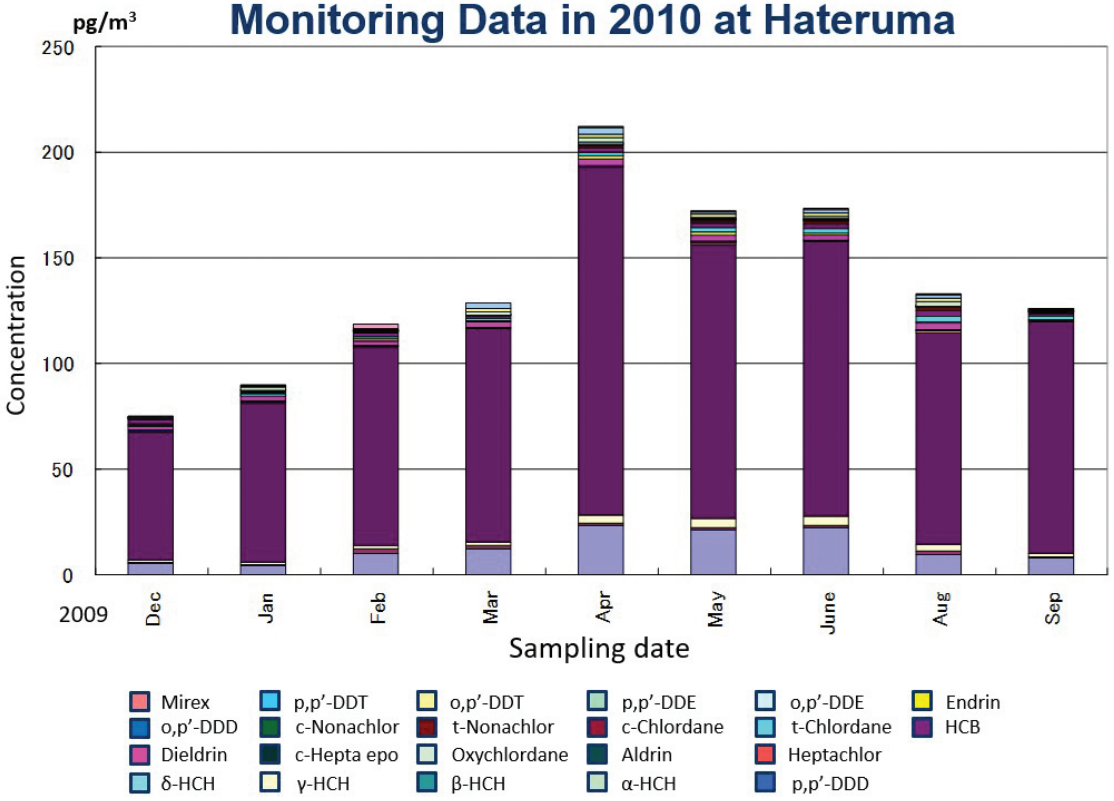
96 hrs on May
HV: 1,000m^3, TD: 2.63m^3

Effect of Humidity



Surrogate recovery (%)
Air temperature: −4.2～12℃
0.5L/min for 6 hrs
13C surrogates: 20 pg

Monitoring Data in 2010 at Hateruma



III–2 <2009-2011>

Cooperative research on bioaccumulation on POPs and relative chemicals

Japan – Noriyuki SUZUKI, Takeo SAKURAI
Korea – Junheon YOON, Byoungcheun LEE, Igchun EOM

1. Background

Bioaccumulation is one of key topic of exposure assessment of POPs and related chemicals which has substantial bioaccumulation potentials. Bioaccumulation is generally assessed by combined information of laboratory experiment, field observation and modeling of bioconcentration and biomagnification. As bioaccumulation is the important topic of concern on the management of POPs in both countries, sharing information and experience of both countries will be important to extend and improve the knowledge of the bioaccumulation.

This cooperative study will focus on the sharing information on bioaccumulation study in both countries. Experimental method and outputs, field observation experiences, and modeling methodologies and outputs will be the topic of research cooperation.

As the current status of the related issues within the Japan-Korea POPs/EDC framework, the project "Cooperative research on fate models on POPs" had been performed during the past several years and its output provides effective basic information of the present project. Based upon the existing scientific achievements in both countries on the related issues, bioconcentration and biomagnifiacation experiments have been conducted in the present project for a variety of POPs and related chemicals, and the results have been shared by the two countries.

2. Research Plan

1) Share information of the bioaccumulation study on POPs and other chemicals between both countries.

2) Share experience on bioaccumulation analysis/modeling of POPs and related chemicals in the aquatic environment.

3) Share experience on bioconcentration experiment of POPs and related chemicals in the aquatic environment.

3. Major Outcomes

The cooperative research conducted a series of laboratory experiments in both of the countries, investigated the two essential processes of bioaccumulation, namely, bioconcentration and biomagnification, of a variety of POPs and the related compounds, and was successful in sharing information and experiences of bioaccumulation studies of these compounds in the aquatic environment.

<KOREA>

1) In the first year, Korea carried out fish bioaccumulation of 9 perfluorinated compounds (PFBS, PFHxS, PFOS, PFOA, PFNA, PFDA, PFUnA, PFDoA, and PFFTA). Blood, liver, kidney, reproductive organ, gills, and muscle tissue were extracted and investigated after a 49-day exposure test (21 days of uptake and 28 days of depuration) using Cyprinus capio.

2) BCF values in fish blood as shown in Table 1 were obtained as a result of calculation according to the OECD TG 305 (Bioconcentration: Flow-through Fish Test). Although blood is a key sample for BCFs studies, BCF values obtained from blood tended to be different from those of other organs.

3) In the 2010 study, Korea tried to interpret the behavior of Deca BDE in the water system environment newly included in the Stockholm Convention using Cyprinus capio. Blood, liver, kidney, birthplace, gills, and muscle tissue were extracted and investigated after a 60-day semi-static exposure test (21 days of uptake and 39 days of depuration).

4) Three exposure groups (control, 5 μg/L, 50 μg/L) were used, and muscle samples were calculated according to OECD TG 305. The BCF value ranged from 0.46±0.12 to 3.86±1.00, resulting in similar results to the BCF value of 4 or less suggested by the WHO.

<JAPAN>

1) A preceding study suggested a considerable contribution of bottom and/or suspended sediment other than the dissolved phase, to the transfer of polychlorinated biphenyls (PCBs) from sediment to fish. These contributions were studied in detail.

The sandworm feeding study confirmed the transfer of sediment associated PCBs to fish via a sediment-dwelling prey. The uptake kinetics were elucidated. In order to evaluate the transfer from sediment to fish, it is necessary to determine the kinetics of sediment-to-sandworm transfer. The depuration rate constants obtained from the sandworm feeding study indicated that the half lives of PCBs may be longer in marbled sole than in freshwater small fishes that are commonly used in laboratory experiments. Using the kinetic parameters obtained in such small-fish studies would result in underestimation of PCB concentrations in marbled sole in the environment.

2) Marine fish are important as food source, but chemical transfer studies therein have been limited. In this study, uptake kinetics, specifically, assimilation efficiency from the dissolved phase by marbled sole, a marine fish, are experimentally determined for the POPs with a range of octanol–water partition coefficient (KOW). Assimilation efficiency is an essential parameter regarding chemical uptake, but have been reported in a limited number of studies.

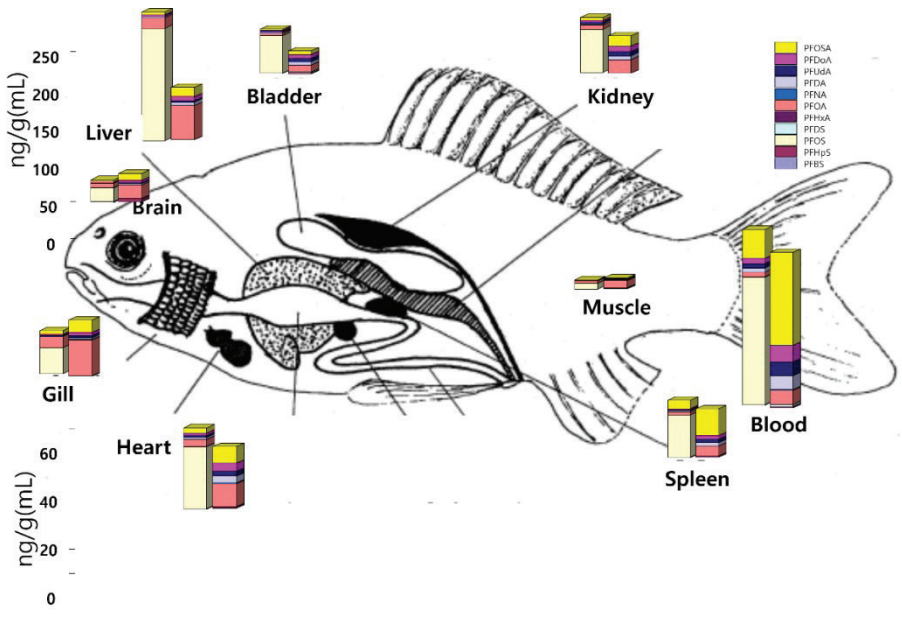
3) The transfer kinetics of polybrominated diphenyl ethers (PBDEs) from sediment to a marine fish, marbled sole, was examined taking into account of debromination of PBDEs in the fish, which was determined by an in vitro hepatic microsomal debromination experiment. Debromination affected the depuration rate of PBDEs, in agreement with in vitro debromination results. PBDE uptake efficiency in the gut was compared between from worm that have taken up PBDEs from sediment, and from sediment in food directly. The former was found to be higher.

Highlight Slides, KOREA

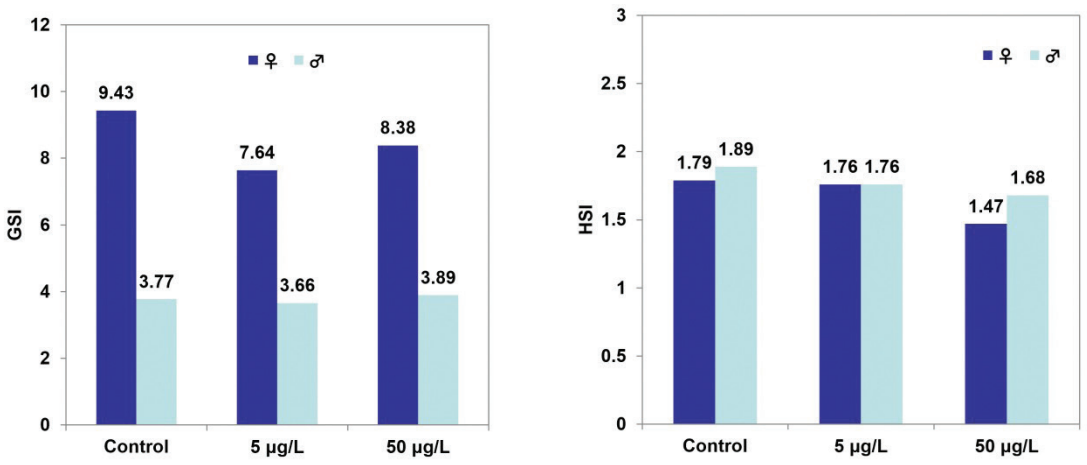
BCF values of seven perfluorinated compounds in fish blood

		BCF ±SD
PFBS	Low	0.18 ±0.18
	High	0.03 ±0.06
PFHxS	Low	144.44 ±40.52
	High	117.80 ±53.88
PFOS	Low	1082.22 ±141.77
	High	798.88 ±268.32
PFOA	Low	16.36 ±5.77
	High	6.68 ±2.23
PFNA	Low	214.96 ±37.68
	High	64.58 ±23.30
PFDA	Low	5664.63 ±432.51
	High	1828.07 ±434.54
PFUnDA	Low	623.24 ±51.19
	High	331.08 ±71.56
PFDoDA	Low	632.25 ±20.91
	High	309.32 ±68.61
PFTrDA	Low	509.97 ±12.16
	High	233.50 ±53.33

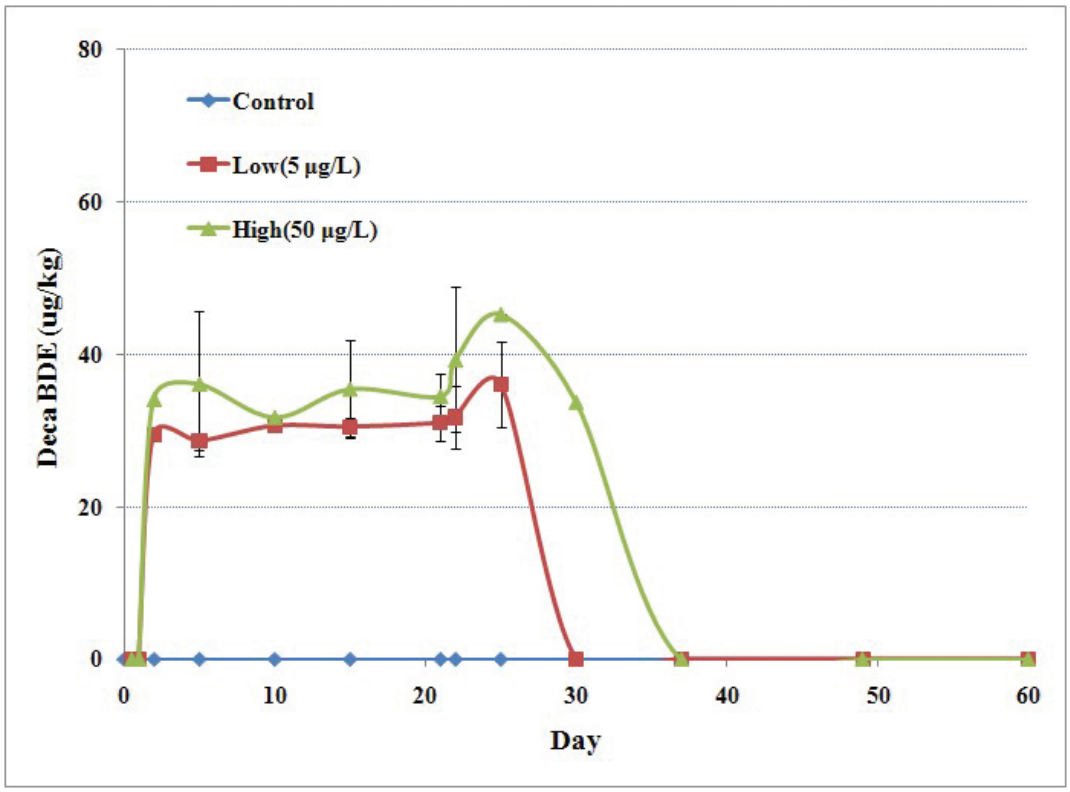
PFCs concentrations accumulated in each organ of Cyprinus capio



Gonadosomatic index (GSI) and Hepatosomatic index (HSI)
of *Cyprinus capio* after 21 days of exposure



Changes in DecaBDE concentrations in muscles over 60 days



PCB food-chain transfer from sediment via sandworm

- Uptake kinetics: Assimilation efficiency (lipid basis)
  - first-order kinetics; control conc subtracted.
  - Similar values reported for freshwater fish.
  - Different trend from passive diffusion model prediction against *K*ow.

$$\frac{\mathrm{d}C'_{\mathrm{b}}}{\mathrm{d}t} = \alpha F C'_{\mathrm{F}} - k_2 C'_{\mathrm{b}}$$

C_b: conc in fish [/g-lipid]
C_F: conc in sandworm [/g-lipid]
α: assimilation efficiency
F: feeding rate [/g-wet fish]
k_2: collective depuration [/d];

* Prime indicates control subtraction.
* Parameters obtained by fitting to the integrated form of the equation.
* Growth dilution corrected.

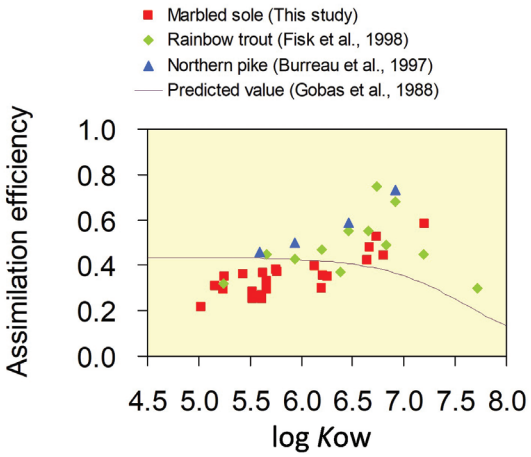


Fig. 6 PCB assimilation efficiency in the gut.

Slide presented at the 9th Joint Symposium on POPs Research (8 March 2010)

POPs transfer to marbled sole, Assimilation efficiencies

$k_i = a_i e_i$
a_i: assimilation efficiency [-]
k_i: uptake rate constant [T^{-1} or $L^3M^{-1}T^{-1}$]
e_i: media exposure rate per unit body mass

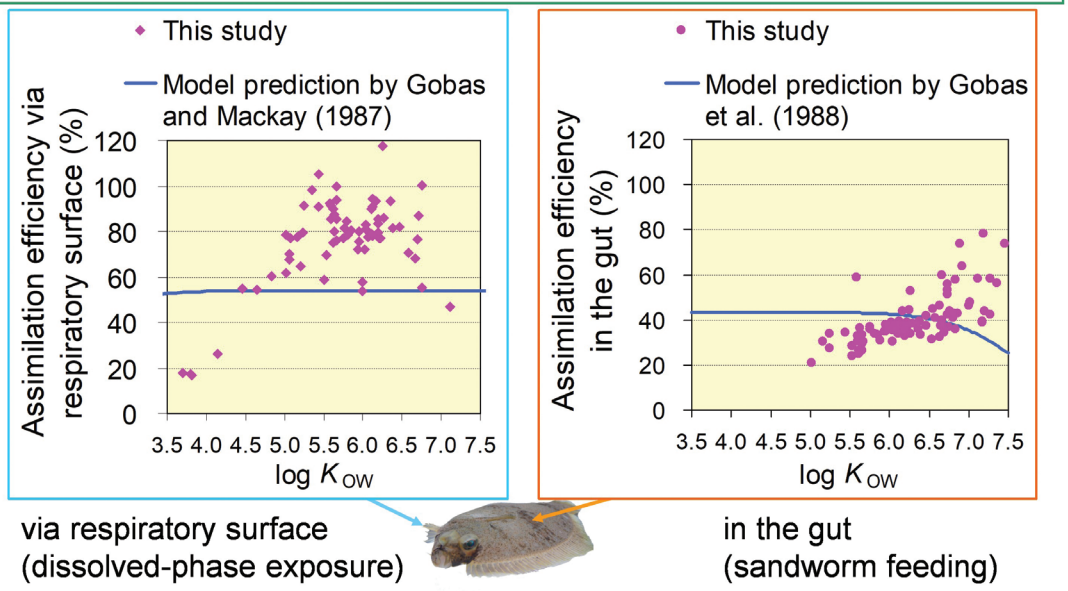
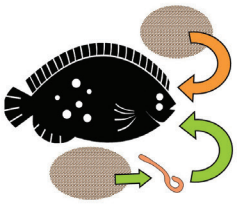


Fig. 6 POPs assimilation efficiency in the respiratory surface and the gut of marbled sole (Kobayashi et al., 2011; Kobayashi et al., in preparation)

Slide presented at the 10th Joint Symposium on POPs Research (15 February 2011)

Direct & indirect PBDE transfer from sediment, Objective



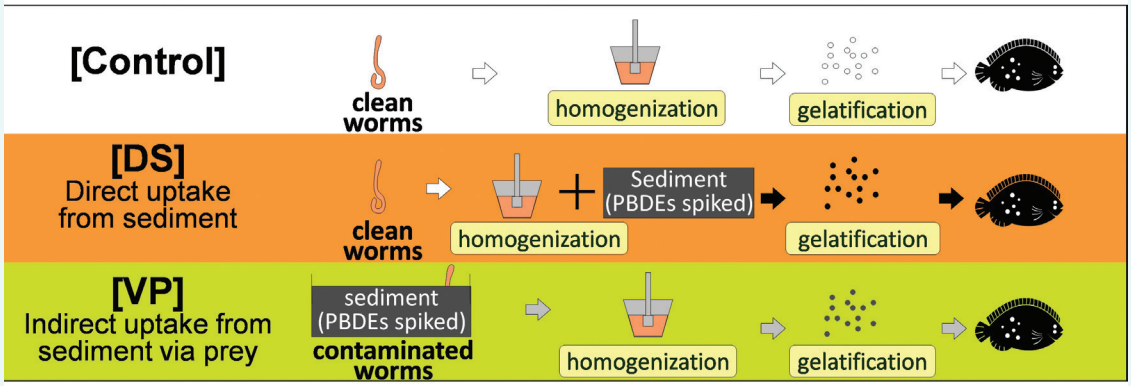
Fish take up POPs in sediment via the gut either directly and indirectly.

Directly [DS]: concomitant intake of sediment particle

Indirectly [VP]: via prey that have taken up POPs from sediment

Objective of the study

- Impact of debromination on PBDE's transfer kinetics
- Difference in PBDE gut uptake between [DS] and [VP]



Slide presented at the 11th Joint Symposium on POPs Research (7 March 2012)

Direct & indirect PBDE transfer from sediment, Result 2

- Debromination affected the depuration rate of PBDEs.
  - BDE99 >> BDE100 [5 Br]; BDE153 > BDE154 [6 Br]
  - Depuration rate constants of PCBs were comparable to previous studies and decreased with increasing K_{OW}.

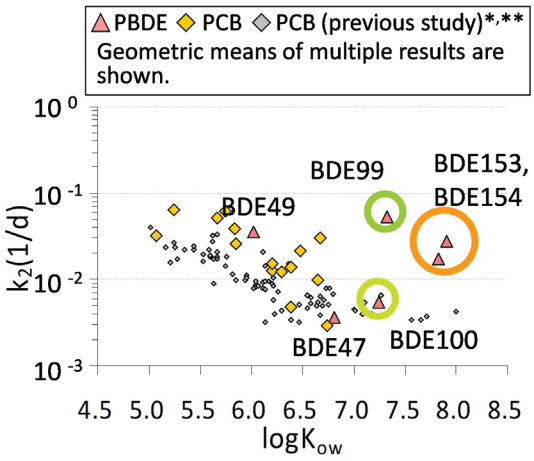
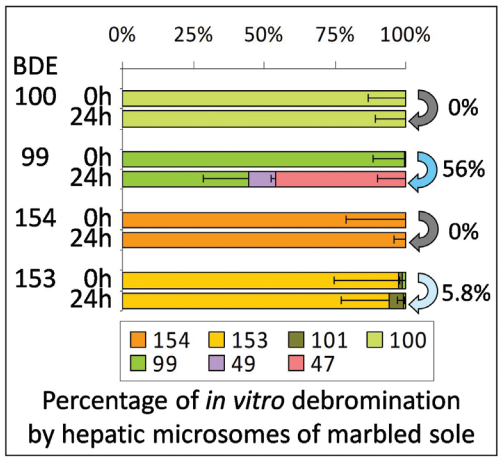


Fig. 2 Depuration rate constants of PBDEs (PCB results shown for comparison)



(Mizukawa et al., in preparation, Kobayashi et al., *2010, **in preparation)

Slide presented at the 11th Joint Symposium on POPs Research (7 March 2012)

III–3 <2009~2011>

Comparison of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) levels in freshwater fish (Crucian carp) between Korea and Japan

Korea - Giho JEONG, Kyunghee CHOI, Narae HWANG, Byoungcheun LEE
Japan - Kiwao KADOKAMI, Tomomi IWAMURA, Yoko KAJIWARA

1. Background

Given that brominated flame retardants are being considered for addition to the Stockholm Convention, which regulates persistent organic pollutants (POPs), we investigated the accumulation of brominated flame retardants using the crucian carp preserved samples used for analysis of dioxins and organochlorine pesticides as samples in order to determine the contamination status before regulation. The targeted flame retardants were polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and tetrabromobisphenol A (TBBPA). If no stored samples remained, the crucian carp were collected and samples were prepared as same as before, then analyzed, and the results were compared between the two countries. Sediments and eggs were also collected and analyzed to determine bioaccumulation, maternal transfer, and resulting sex differences.

2. Research Plan

1) To understand the distribution characteristics and bioaccumulation status of brominated flame retardants in freshwater fish.

2) To select PBDEs, HBCDs and TBBPA as target substances

3) To elucidate the causes of differences in contaminant levels between sampling sites and both countries.

4) To study harmonization about sampling, measurement and analysis between Korea and Japan.

3. Major Outcomes

< KOREA>

1) The concentrations of PBDEs in male and female crucian carp were 6.5 - 225 (median: 62) and 1.3 - 725 (median: 46) ng/g lipid wt in the muscle, respectively. Tetra-BDEs and deca-BDEs were the main congeners, accounting for 47% and 26% of the total PBDEs concentration, respectively, followed by penta-BDE (10%), nona-BDE (8.1%), and hexa-BDE (4.2%). Among tetra-BDEs, BDE-47 was the main isomer and accounted for 91% of total tetra-BDE.

2) ∑HBCDs in male and female carp were 2.5 - 76 (median, 7.9) and 1.7 - 31 (median, 8.4) ng/g lipid wt, respectively. The concentration of ∑HBCD in the eggs was lower than in the muscles of male and female. In oviparous organisms, hydrophobic substances present in females are known to be transferred to eggs along with lipid components. The ratios of α-, β-, and γ-HBCDs to total HBCDs concentration were 76%, 9.0%, and 15% in female muscle, respectively; 80%, 7.1%, and 13% in male crucian muscle; and 69%, 18%, and 13% in eggs. The preferential absorption of α-HBCD into the body and the bioisomerization process of γ-HBCD are thought to be the reasons why α-HBCD becomes the main component in crucian carp.

3) The concentrations of HBCDs were much higher than of TBBPA in both carp and sediment. In Korea, the distribution volumes of HBCDs and TBBPA in 2006 were 2,686 and 32,687 tons, respectively. Although TBBPA is much more abundant, the reason why its concentration was lower than HBCDs appears to be due to the following factors. (1) Since TBBPA is chemically bonded to the polymer medium, the leakage rate into the environment is lower than that of HBCDs. (2) Because TBBPA is more polar than HBCDs, bioaccumulation and accumulation of organic substances in sediments are more difficult than HBCDs. (3) TBBPA has a property of binding well to proteins produced in vivo, so its extraction efficiency is lower than that of HBCDs.

<JAPAN>

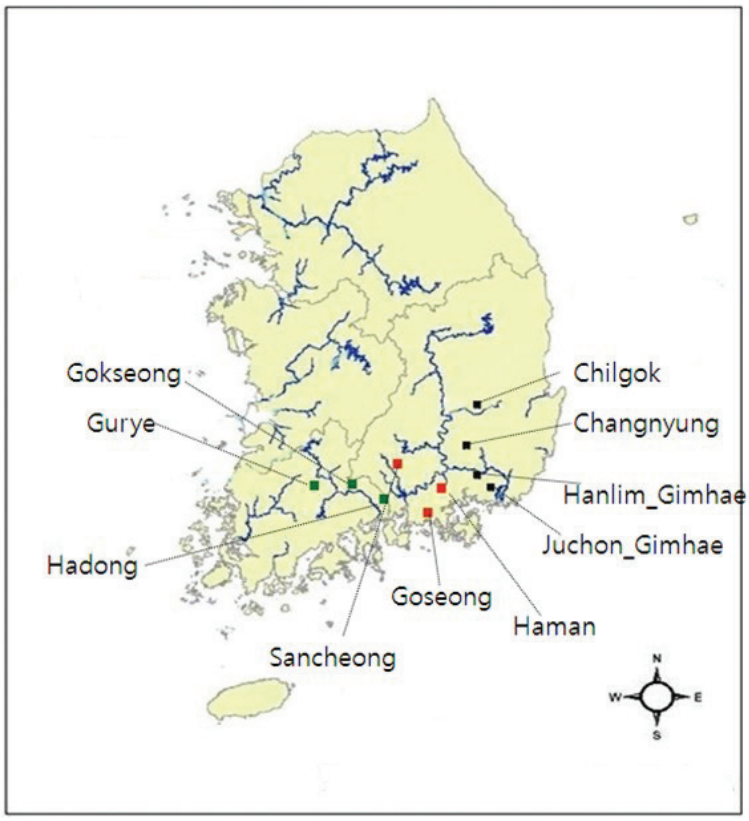
1) PBDEs concentrations of crucian carp in Japan were 2.4-159 ng/g lipid wt. (mean=38.1, geometric mean=15.9). PBDEs were detected at high concentrations in the large-cities; concentrations in the agricultural areas and the remote areas were significantly lower than at other areas. Tetra-BDEs were the dominant homologue in the fish. Higher brominated PBDEs were dominant in sediment. Difference of distribution ratio of PBDEs between sediment and fish seems to be due to low bioavailability of higher brominated ones. Sex difference in PBDEs concentration was found like other POPs during the spawning season because of maternal transfer. One-fifth of PBDEs in the female transfer to the eggs.

2) HBCDs concentrations of crucian carp in Japan were 5.7-15,000 ng/g lipid wt. (mean=1,200, geometric mean=68). HBCDs were detected at high concentrations in the large-cities; concentrations in the agricultural areas and the remote areas were lower than at other areas. Spatial distribution of HBCDs and PBDEs shows a similar trend. α- and γ-HBCD were dominant in the fish. Sex difference in HBCDs concentration was smaller compared with other POPs during the spawning season. Maternal transfer rate of HBCDs was lower than other POPs.

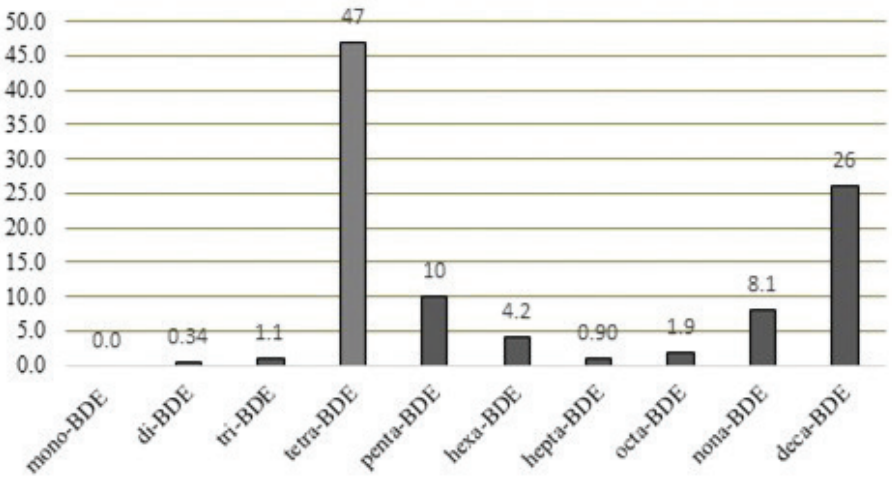
3) Although the production or consumption amounts of TBBPA are the largest among brominated fire retardants, its concentrations in crucian carp were very low and spatial difference was not found, which indicates that TBBPA is hard to accumulate in fish.

Highlight Slides, KOREA

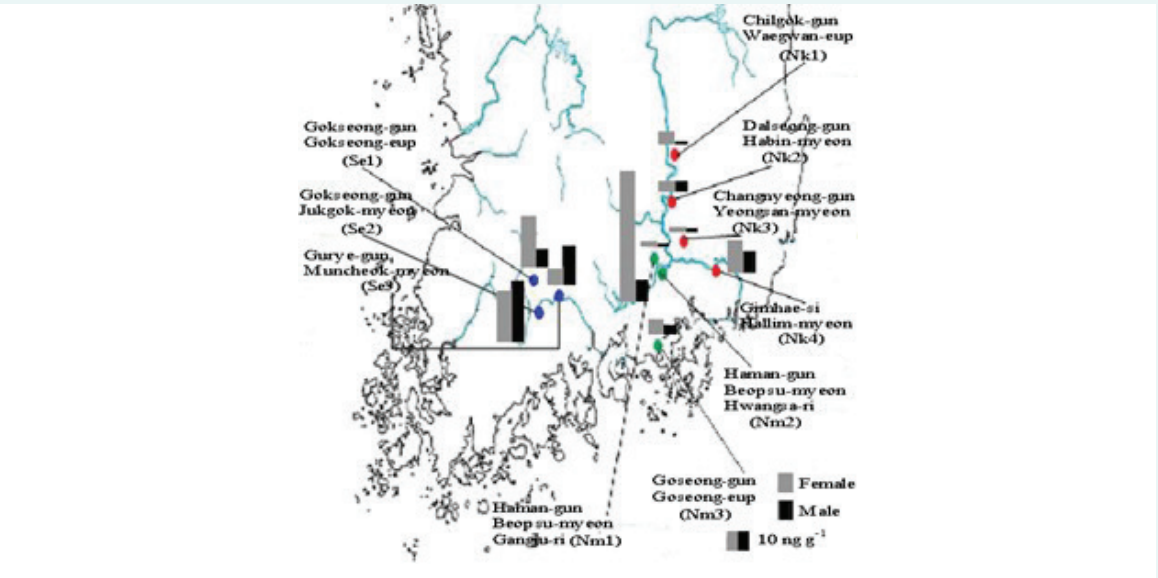
Locations of sampling sites (PBDEs), Korea.



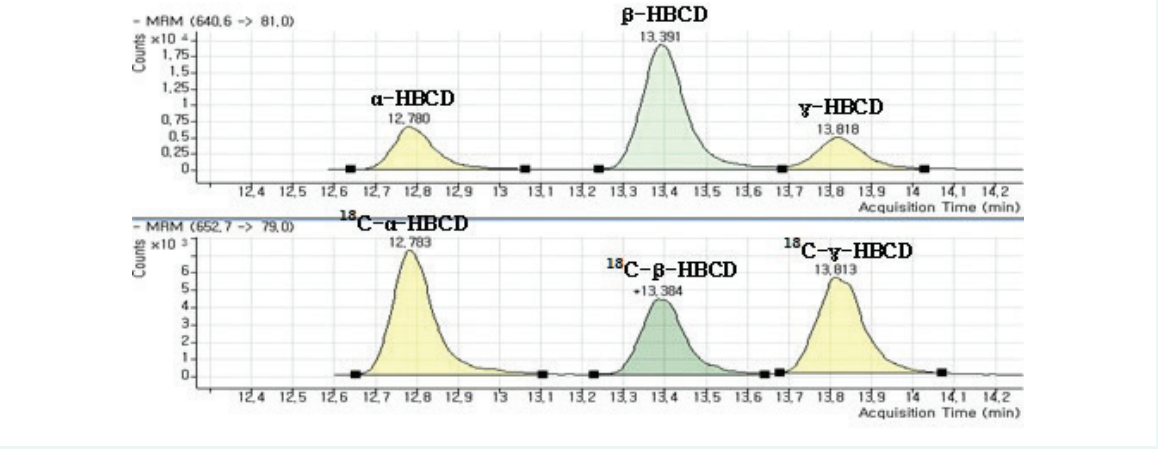
Relative distribution of PBDE homologs (%)



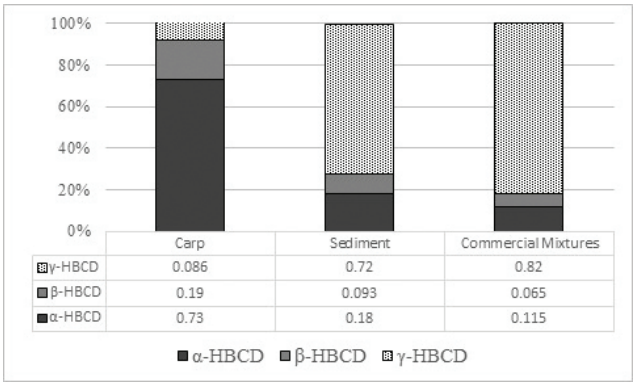
Sampling sites and ∑HBCD levels in crucian carp (126°–130° E; 34°–38° N)



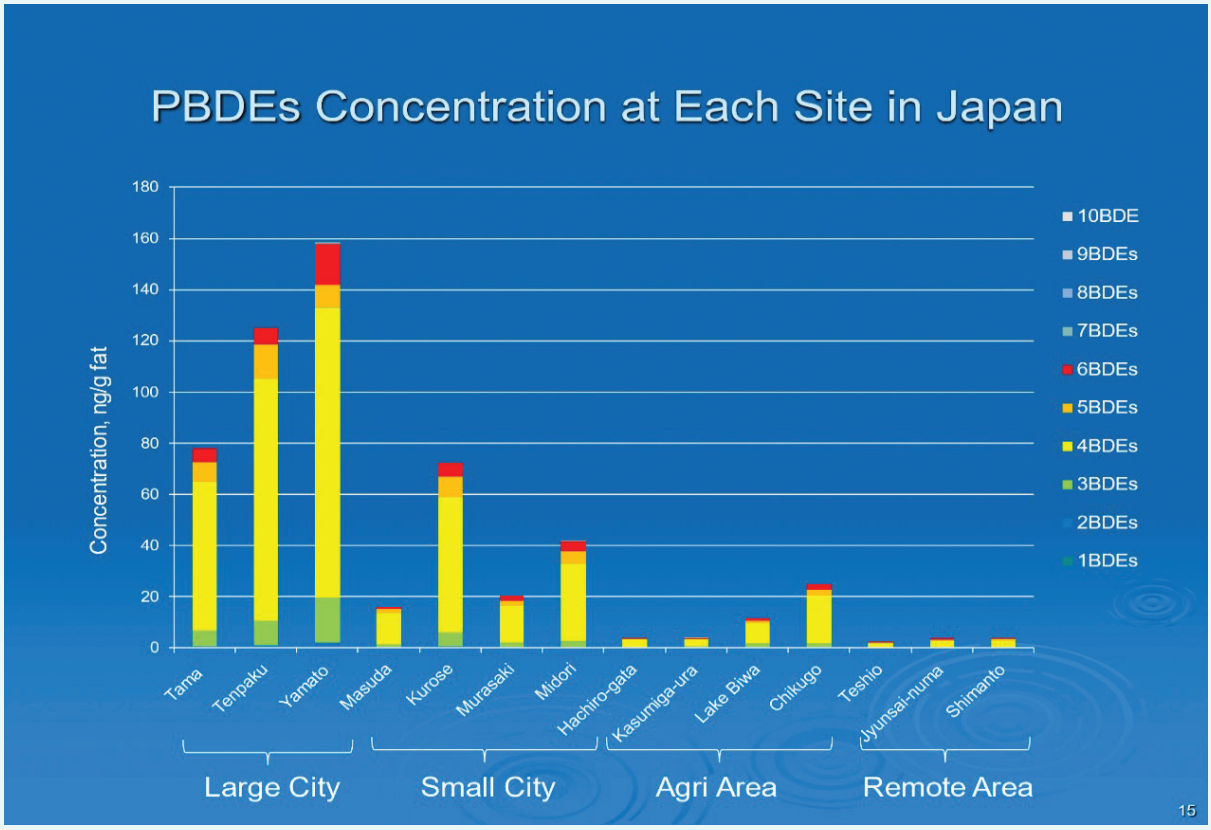
LC-MS/MS chromatograms of native and labelled α-, β-, and γ-HBCDs.

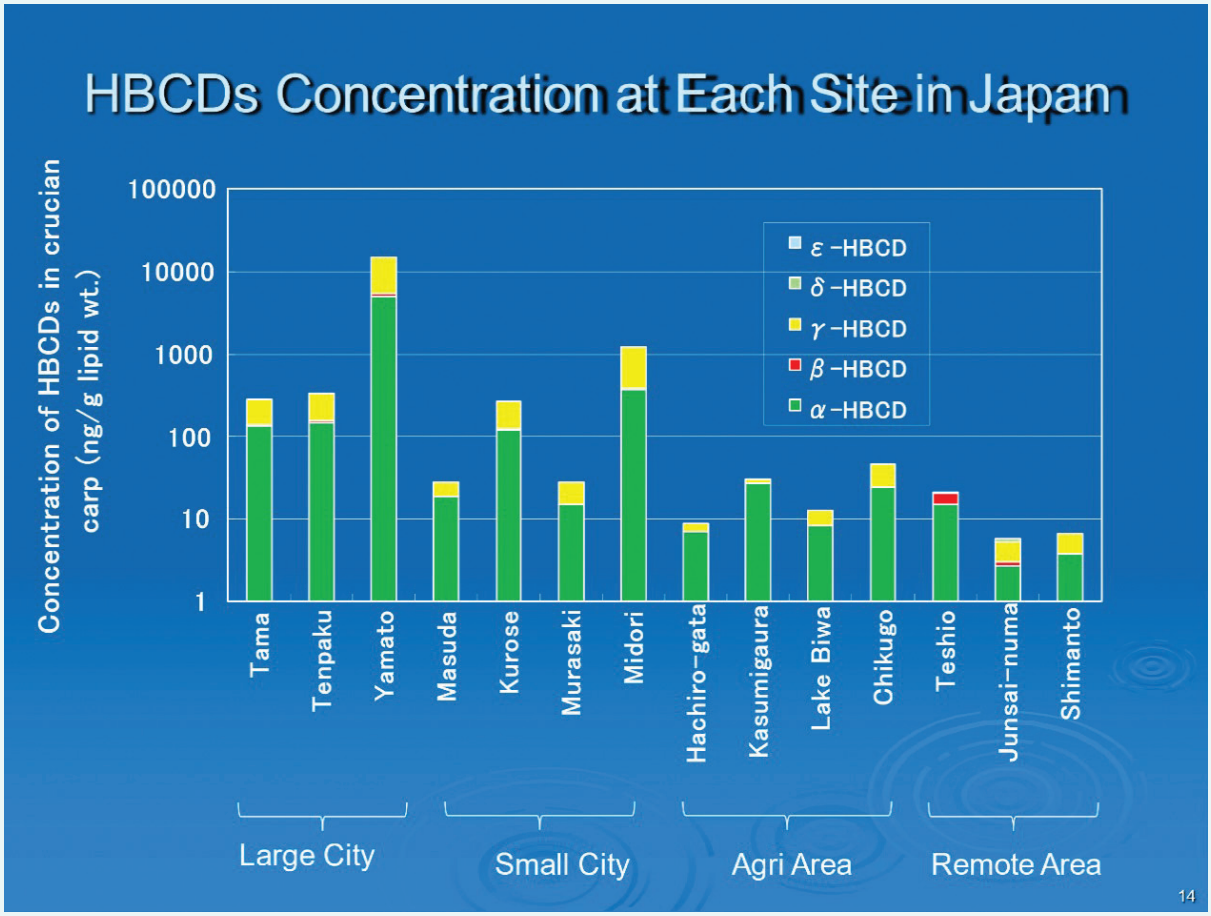


Average distribution ratio of HBCD diastereomers to the ∑HBCD ccumulated in crucian carp and sediments, and commercial mixtures.



	Carp	Sediment	Commercial Mixtures
γ-HBCD	0.086	0.72	0.82
β-HBCD	0.19	0.093	0.065
α-HBCD	0.73	0.18	0.115


PBDEs Concentration at Each Site in Japan
Concentration, ng/g fat
180
160
140
120
100
80
60
40
20
0
10BDE
9BDEs
8BDEs
7BDEs
6BDEs
5BDEs
4BDEs
3BDEs
2BDEs
1BDEs
Tama
Tenpaku
Yamato
Masuda
Kurose
Murasaki
Midori
Hachiro-gata
Kasumiga-ura
Lake Biwa
Chikugo
Teshio
Jyunsai-numa
Shimanto
Large City
Small City
Agri Area
Remote Area
15


HBCDs Concentration at Each Site in Japan
Concentration of HBCDs in crucian carp (ng/g lipid wt.)
100000
10000
1000
100
10
1
ε -HBCD
δ -HBCD
γ -HBCD
β -HBCD
α -HBCD
Tama
Tenpaku
Yamato
Masuda
Kurose
Murasaki
Midori
Hachiro-gata
Kasumigaura
Lake Biwa
Chikugo
Teshio
Junsai-numa
Shimanto
Large City
Small City
Agri Area
Remote Area
14

TBBPA Concentration at Each Site in Japan

24

Sexual Difference in Concentrations and Maternal Transfer During the Spawning Season

Compound	Male	Female	Egg	Transfer ratio, %
Dioxins	1.2	1	0.59	21
DDTs	1.7	1	0.60	25
Chlordanes	1.4	1	0.54	23
Drins	1.6	1	0.95	34
Heptachlors	1.5	1	0.74	28
HCB	1.2	1	0.77	30
Mirex	1.4	1	0.64	26
HCHs	1.5	1	0.60	26
PBDEs	1.4	1	0.51	21
HBCDs	0.97	1	0.28	12
TBBPA	(2.4)	1	(0.81)	(39)

DDT; p,p'- & o,p'-DDT, p,p'- & o,p'-DDE, p,p'- & o,p'-DDD; Chlordanes: trans- & cis-chlordane, trans- & cis-nonachlor, oxychlordane; Drins: aldrin, endrin, dieldrin; Heptachlor: heptachlor, trans- & cis-heptachlor epoxide; HCHs: α-, β-, γ- & δ-HCH

29

III–4 <2009~2011>

Comparison of monitoring data for perfluorinated chemicals between Japan and Korea

Japan – Norihisa TATARAZAKO, Norimitsu SAITO, Kazuaki SASAKI
Korea - Igchun EOM, Hyunmi KIM, Junheon YOON, Jaean LEE, Byoungcheun LEE, Hyeonseo CHO

1. Background

Perfluorinated chemicals like PFOS and PFOA are persistent in the environment and have been shown to bioconcentrate in aqua-organism. It has been detected in a number of species of wildlife, including marine mammals. Its persistence, presence in the environment and bioaccumulation potential indicate cause for concern. The result of reproduction study of the Daphnia which we performed last year showed that its toxicity is not high. However, because we do not examine the impact except the short term exposure, it is necessary to conduct low level long term exposure research in order to reveal their ecological negative effects in detail. On the other hand, perfluorinated chemicals have been detected not only in sediment downstream of a sewage plants but in the river water by our investigation last year. Given the apparent widespread occurrence of perfluorinated chemicals, national or regional exposure information gathering from soil, water, sediment, biota and risk assessment may need to be considered. Korea and Japan cooperate to monitor the amounts of perfluorinated chemicals from several media and living materials in both countries. Several toxicity experiments will be performed. With monitoring results from both countries and relevant toxicity data, the risk assessment of the perfluorinated chemicals will be performed.

2. Research Plan

1) Common ownership and development of the monitoring technique between Japan and Korea

2) Common ownership of the toxic data of Perfluorinated chemicals using aquatic animals between Japan and Korea.

3) Information sharing of the low level long term exposure study

4) Start investigation on the risk of not only PFOS/PFOA but also other fluorinated chemicals.

3. Major Outcomes

1) PFOS is a major chemicals in environmental media. The concentration level of PFCs in domestic and livestock waste water treatment system is lower than industrial regions. Based

on the data, main environmental sink of PFCs is water. A lot of PFCs are not officially used. But concentration levels in Industrial regions showed that a lot of unknown PFCs were used.

2) 7-day LC50 and 14-day LC50 in earthworm showed that Acute toxicity of PFOS is 3 times higher than PFOA. 96hr LC50of PFOA and PFOS to melanian snail (*Semisulcospira gottschei*) is 238.1 mg/L and 64.8 mg/L, respectively. Prolonged exposure of PFOA showed that it has no significant effect to growth rate in melaniansnail. But histological effects like necrosis or thickness decrease in epithelium were showed in mantle, foot, and hepatopancrease.

3) PFCs were detected in rivers water samples in IWATE (> 0.01ng/L) Perfluorosulfonates: PFBS, PFHxS and PFOS, Perfluorocarboxylates: PFHxA, PFHpA, PFOA, PFNA, PFDA and PFUnDA.

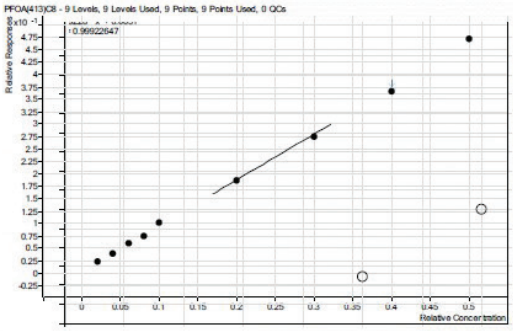
4) Composition ratio of PFCs in the stream water was as follows; PFOA(8) ≈ PFNA(C9) > PFOS(8) > PFDA(C10) > PFUnDA (C11). Bioaccumulation factor of PFCs in Medaka was as follows;

Bowel-female (710) > Bowel-male (650) > muscle-female (550) > muscle-male (400) > egg (320)

a) HPLC	
Instrument	Agilent 1200 Series
Analytical column	ZORBAX Edipse Plus C18 (2.1mm x 100mm, 1.8 μm)
Column temp.	40 ℃
Mobile phase	A: 10 mM CH_3COONH_4/H_2O
	B: CH3CN (LC/MS grade)
Injection volume	10.0 μL

b) LC/MS/MS	
Instrument	Agilent 6410
Ionization	ESI (Negative mode) , SRM
Prec. Ion	M-1
Product Ion	M-45 (Perfluorocarboxylic acids)
	80, 99 (Perfluorosulfonic acids)
Frag. Voltage	50-100 (Perfluorocarboxylic acids)
(v)	150-200 (Perfluorosulfonic acids)
CE	5 (Perfluorocarboxylic acids)
(v)	55 (Perfluorosulfonic acids)
Drying gas	N2 (5 L/min, 350 ℃)
Vaper Temp.	180 ℃
Nebulizer	N2 (60 psi)
Capillary	2000 v
Delta EMV	400 v

c) Gradient		
Time [min]	Frow rate [mL/min]	Solv. A [%]
0	0.2	70
4	0.2	70
20	0.2	25
25	0.2	25
26	0.3	10
34	0.3	10
35	0.2	70
45	0.2	70



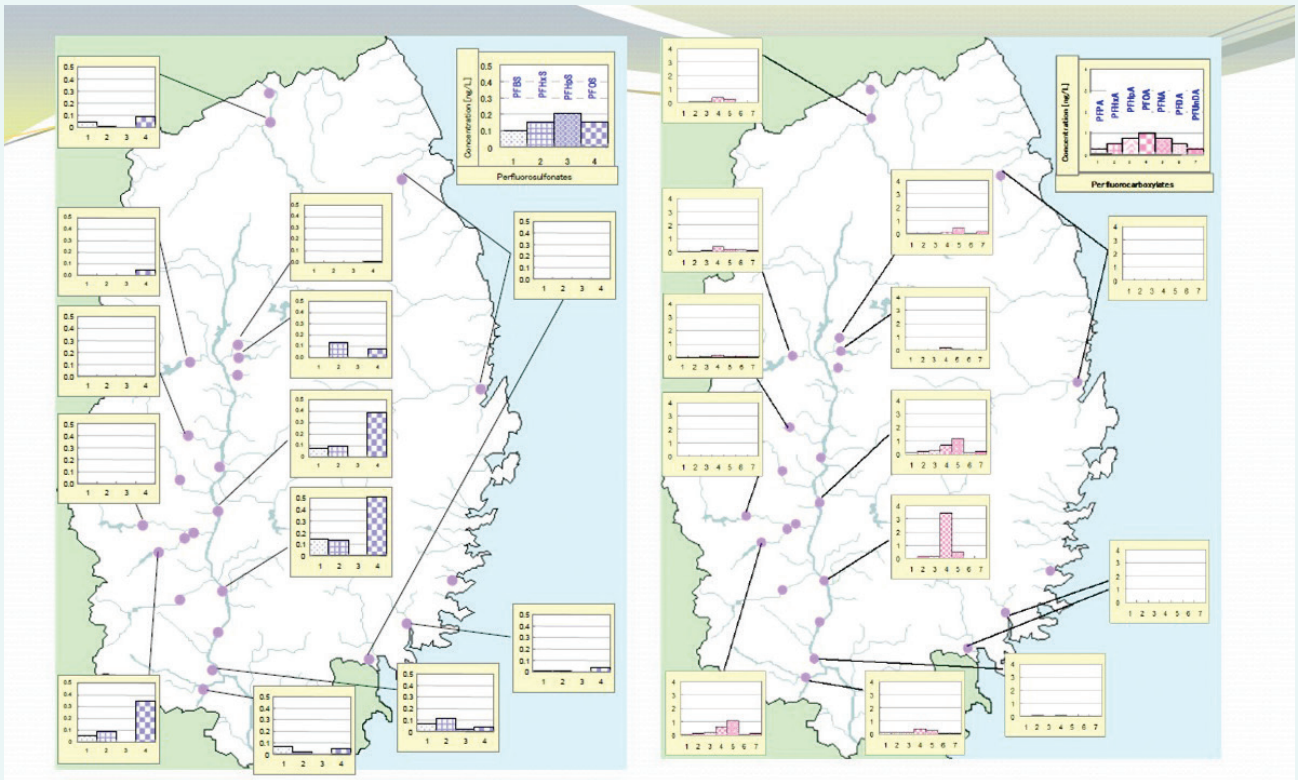
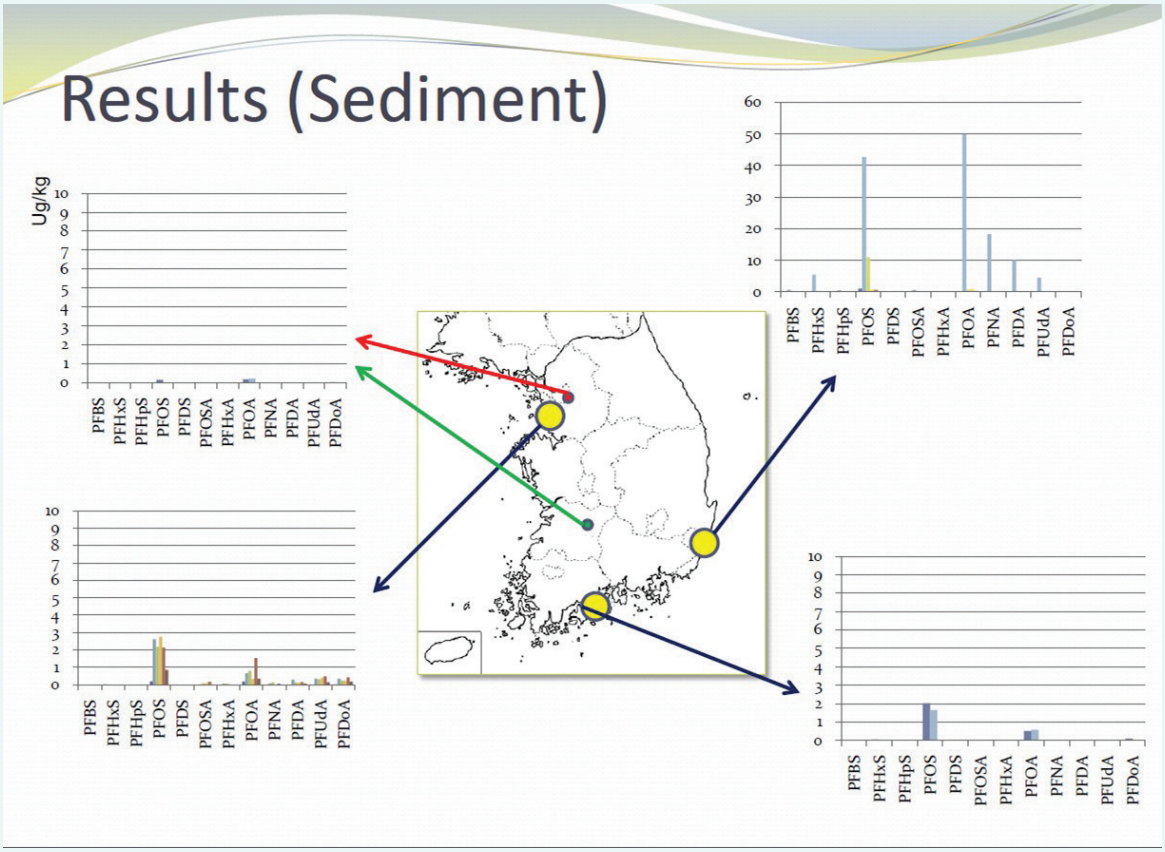
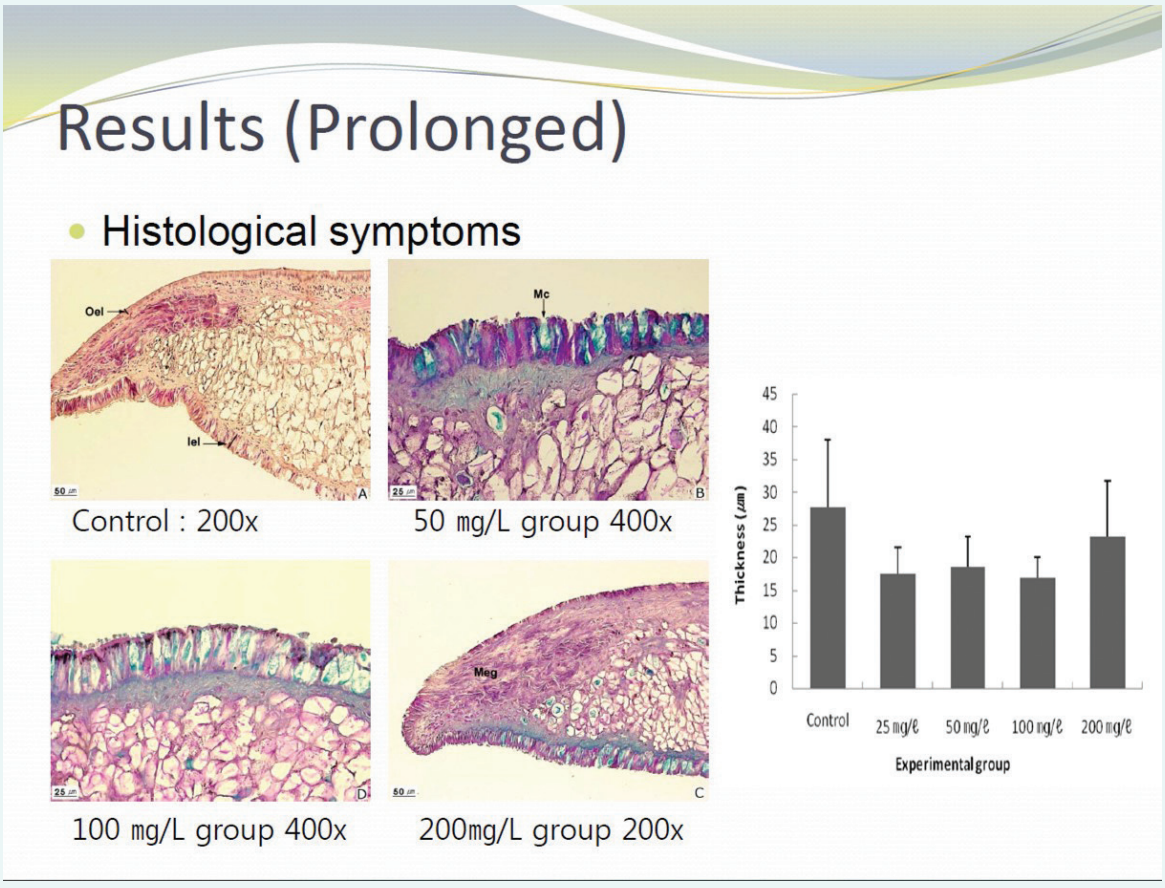
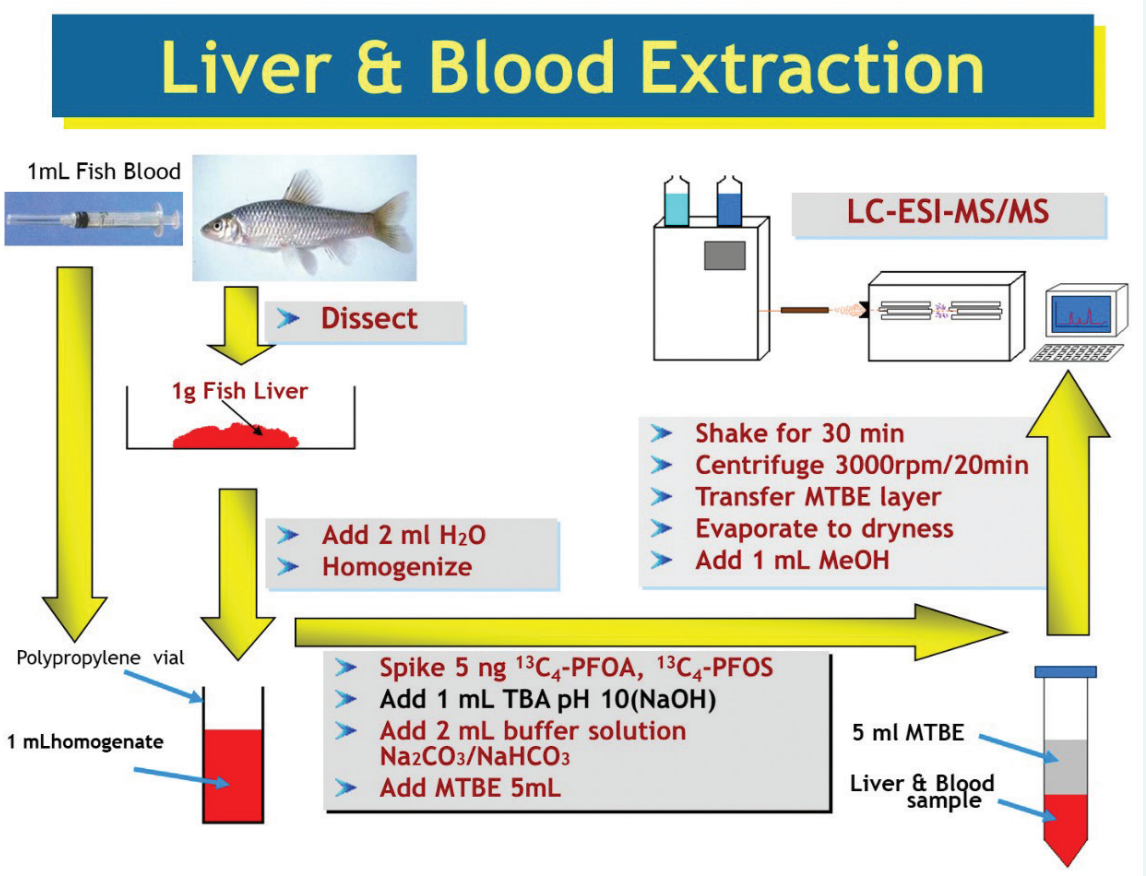


Fig.3 PFCs Concentrations in River Water in IWATE(2009)


Results (Sediment)
Ug/kg
PFBS
PFHxS
PFHpS
PFOS
PFDS
PFOSA
PFHxA
PFOA
PFNA
PFDA
PFUdA
PFDoA


Results (Prolonged)
Histological symptoms
Oel
Iel
Mc
Meg
A
B
C
D
Control : 200x
50 ㎎/L group 400x
100 ㎎/L group 400x
200㎎/L group 200x
Thickness (㎛)
Control
25 ㎎/ℓ
50 ㎎/ℓ
100 ㎎/ℓ
200 ㎎/ℓ
Experimental group

* Survey area
  * Lake Chungju
  * Bokha stream
* Period
  * 1st 2010. 6. 17, 2nd 2010. 9. 17
* Sampling Method :
  * water : 1L Polypropylene bottle(pre-cleaned with MeOH and Milli-Q water)
  * Sediment : 250mL Polypropylene bottle(pre-cleaned with MeOH and Milli-Q water)
  * Suspended solid
  * Phytoplankton, Zooplankton
  * Fishes(*Carassius auratus*(Carp) , *Siniperca scherzerii* (Mandarin))



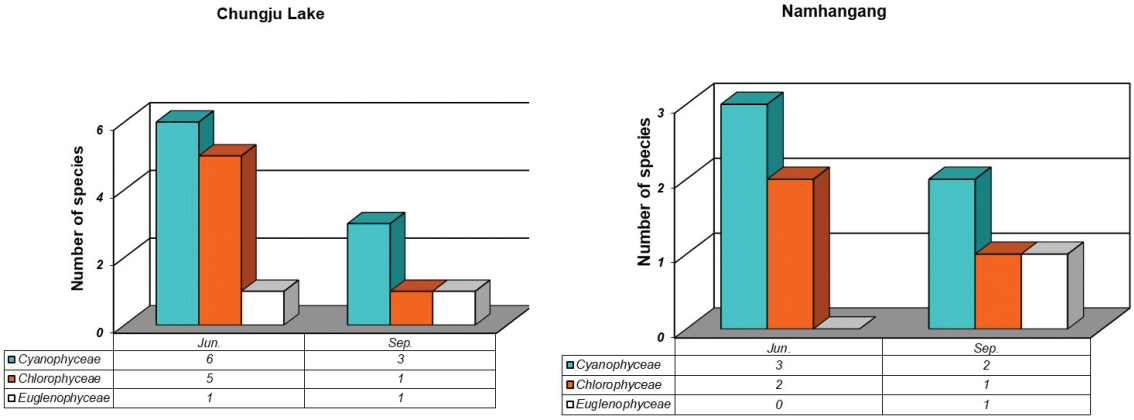


Fig. The number of phytoplankton species occurring in Chungju lake and Bokha stream.

Residual characteristics of PFCs in target Ecosystem

matrix		water	Suspended Solid	sediment	plankton	carp blood	mandarin blood	carp liver	mandarin liver
unit		ng/L	ng/g dry-wt.	ng/g dry-wt.	ng/g	ng/mL	ng/mL	ng/g wet-wt.	ng/g wet-wt.
PFCA	C5	<0.1	<0.1	<0.02	<0.1	<0.1	<0.1	<0.1	<0.1
	C6	<0.1	<0.1	0.007±0.016	<0.1	<0.1	<0.1	<0.1	<0.1
	C7	0.27±0.19	<0.1	0.011±0.021	<0.1	<0.1	<0.1	<0.1	<0.1
	C8	0.20±0.31	14.56±17.99	0.071±0.082	<0.1	0.25±0.32	0.19±0.04	0.06±0.11	0.19±0.08
	C9	0.08±0.16	1.85±3.70	0.023±0.04	0.29±0.17	2.83±3.89	0.19±0.27	0.01±0.00	<0.1
	C10	0.03±0.05	4.58±6.67	0.029±0.027	0.03±0.11	7.14±3.57	13.23±8.78	1.05±0.48	1.67±1.58
	C11	<0.1	3.00±6.01	0.043±0.031	0.13±0.15	15.62±12.64	20.32±11.42	1.69±0.80	4.54±1.70
	C12	<0.1	3.52±5.23	0.022±0.014	0.36±0.41	8.23±5.75	6.79±3.55	1.01±0.56	1.79±0.62
	C13	<0.1	<0.1	0.021±0.017	0.24±0.32	6.39±7.03	9.73±6.22	0.71±0.48	3.10±0.86
	C14	<0.1	<0.1	<0.02	0.12±0.23	1.66±1.50	1.65±0.88	0.27±0.24	0.61±0.18
	C16	<0.1	<0.1	<0.02	0.02±0.05	0.05±0.12	0.01±0.05	<0.1	<0.1
PFSA	C4	5.33±7.02	<0.1	<0.02	<0.1	<0.1	<0.1	0.03±0.17	<0.1
	C6	2.03±1.69	<0.1	<0.02	<0.1	0.04±0.06	<0.1	0.01±0.00	<0.1
	C7	<0.1	<0.1	<0.02	<0.1	<0.1	<0.1	0.65±0.63	5.25±6.93
	C8	3.30±2.92	54.15±48.41	0.178±0.127	2.07±4.59	35.72±38.30	60.62±75.95	15.14±11.38	19.38±33.10
	C10	<0.1	<0.1	<0.02	<0.1	0.12±0.18	0.43±0.37	0.12±0.14	0.01±0.00

IV-1 <2012~2014>

Harmonization between Korea and Japan of Analytical Methods for Dioxins and Existing/new POPs

Korea - Samcwan KIM, Kyunghee CHOI, Jongwoo CHOI
Japan - Yasuyuki SHIBATA, Yoshikatsu TAKAZAWA

1. Background

Article16 of the Stockholm Convention requires the Parties to conduct environmental monitoring of priority media, including air, and submit "comparable" monitoring data to the Convention in an effort to reduce global contamination by POPs, such as dioxins, PCBs and organochlorine pesticides. As a joint research theme in this bilateral program, a harmonized POPs air monitoring method has been developed and used in both countries to obtain data on POPs in remote areas, which were informed in the first Regional Report on the Effectiveness Evaluation of the Stockholm Convention in the Asia-Pacific region.

Meanwhile, ten new chemicals including endosulfan were finally added to the Convention by the POPs Review Committee. It is necessary, therefore, for the Parties to establish monitoring methods of the additional POPs together with the 12 original POPs in order to conduct environmental monitoring and report data for the next effectiveness evaluation.

To address the needs mentioned above and prevent global contamination by POPs and other related chemicals, Japan and Korea will continue to develop precise and accurate monitoring methods, including both sampling system and analytical instrumentation as well as QA/QC protocols, in order to conduct monitoring in both countries and play a key role together in research and development of regional/global POPs monitoring for other Asian countries.

Japan and Korea have already banned the usage of the OCPs decades ago, some pesticides are still detected in the ambient air. For example, HCB has showed the highest detection frequency and concentration among the POPs in the ambient air, but studies on major sources of HCB are insufficient. Environmental forensic science research is necessary to suggest measure for reducing POPs.

2. Research Plan

1) Compile information on new POPs sampling and analytical methods in the air with QA/QC procedures for harmonizing methods in both countries.

2) Continue optimization of the automated POPs sampler for air monitoring.

3) Develop analytical methods of stable isotopes ratio for tracing POPs in environmental forensic science.

4) Develop and apply new techniques, such as GC/MSMS and thermal desorption devices, for the monitoring.

3. Major Outcomes

<KOREA>

1) According to existing research results, chiral contaminants that are not affected by biological processes exist as a racemic mixture and EFs are close to 0.5, but when exposed to biological processes such as microbial decomposition, chiral contaminants undergo selective decomposition.

2) The EFs of o,p'-DDD were 0.51 in coastal areas and 0.62 in inland areas, showing a large difference between the points. Therefore, the origin of o,p'-DDD in coastal areas has moved from a recent source of pollution, and the origin of o,p'-DDD in inland areas is presumed to be DDT used in the past.

3) Harmonization of POPs analytical method at ambient reviewed PFCs and HCHs, PeCB, Endosulfanes as new POPs, and found that the atmospheric sampling rate was 225-750 LPM in Korea, while it was 700 LPM in Japan, and RRF was 700 LPM in Korea (15%) and Japan (15%) showed a difference

<JAPAN>

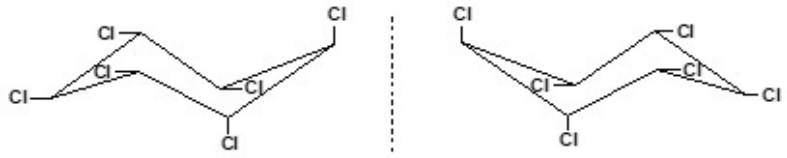
1) TD-GCxGC-MS/MS showed a potential as same as HV-GC/HRMS in airborne POPs detection.

2) Findings on thermal desorption analysis for POPs:

- There is little memory effect on the device. Empty analysis immediately after analysis of STD and actual sample and analysis with only solvent introduced, results are at blank level in both cases.
- Solvent introduced into the TD has no effect on the recovery rate. No change in recovery was observed when solvent was added to the TD liner during STD analysis.
- The recovery rate increases when the flow rate during aspiration is reduced. Increasing the flow rate significantly increases the amount of POPs that break through.
- Tenax adsorbent is more suitable than carbon adsorbent. With carbon-based adsorbents, large moisture-derived interference peaks are observed during analysis, making accurate quantification difficult.

3) It is expected that the automatic air sampler with the TD-technique promotes data storage of airborne POPs at remote area where the replacement of adsorbents is geographically hard.

Chiral OCPs



(+) enantiomers of α-HCH
$C_6H_6Cl_6$

(-) enantiomers of α-HCH
$C_6H_6Cl_6$

Fig. Chemical structures of some hexachlorocychlohexaneisomers

- Ef = $(A_+)/(A_+ + A_-)$
- Microorganism Exposure : Efs > 0.5(racemic) > Efs

(Finizio *et al.*, 1998; Harner *et al.*, 2000; Bidleman *et al.*, 1999; Hung *et al.*, 2002).

❖ **EFs of chiral OCPs in ambient air of coastal and inland site**

Site	HEPT	HEPX	TC	CC	MC-5	OXY	o,p'-DDT	o,p'-DDD
C-1	-	0.74	0.50	0.46	0.48	0.50	0.51	0.51
C-2	-	0.71	0.47	0.40	0.52	0.55	0.50	0.50
C-3	-	0.70	0.49	0.46	0.46	0.54	-	0.51
I-1	-	-	0.50	0.49	0.48	-	-	-
I-2	-	0.74	0.48	0.46	0.50	0.63	0.57	0.62
I-3	-	0.71	0.46	0.49	0.49	0.56	0.50	-

❖ New POPs : HCHs, PCB, Endosulfanes

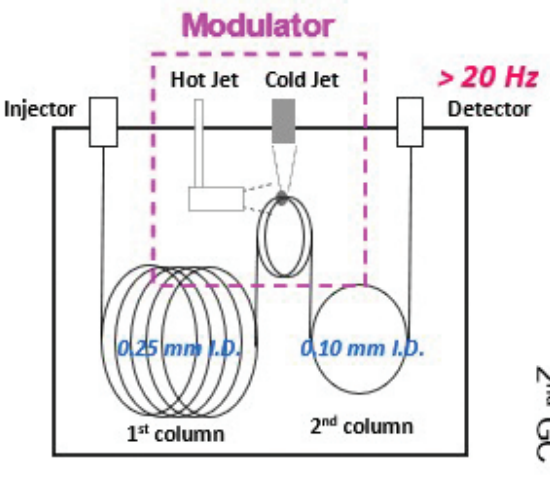
Korea	Japan
☐ Sampling o Duration : 24 hrs o Repeat : 3 times o Aspiration Speed : 225 ~ 750 LPM o Adsorption Media : QFF, PUF, XAD or ACF o Instrument : HVAS o Surrogates : ^{13}C POPs	☐Sampling o Duration: 24hrs o Repeat: 3times o Aspiration Speed : 700L/min o Adsorption Media : QFF, PUF, ACF o Instrument: HVAS o Surrogates: ^{13}C POPs
☐ Calibration Curve o Standard Soln. : CS1 ~ CS5 o r^2 : 0.99 - RRF : RSD ±15% - Verification : CS3 ±20%	☐Calibration Curve o Standard Soln.: 1.0 - 400 pg/uL (PBDEs) 0.4 - 800 pg/uL (PeCB)

-continued-

Korea	Japan
☐ Recovery Rate : 40~120%	
☐ MDL Confirmation o EDL (Estimated Detection Limit)	☐ MDL Confirmation o Blank check and EDL
☐ HRGC/HRMS o Resolution : 10% valley above 10,000 o PFK : 5 ppm o Isotope Ratio : ±15% o Lock Mass Stability : ±20%	☐HRGC/HRMS o Resolution : 10% valley above 10,000 o PFK: 5 ppm o Isotope Ratio : ±15% o Lock Mass Stability: ±20%
☐ QA/QC in Laboratory o MDL, Accuracy , Precision : 1 time/year - MDL : 7 times, SD x 3.14 - Accuracy : Recovery Rate - Precision : RSD	☐QA/QC in Laboratory o MDL. Accuracy, Precision : 3 times/year o MDL: 7times SDx3.14 o Accuracy: Recovery o Precision: RSD
☐ Unit : 0 ℃, 1 atm	☐Unit: 0 ℃, 1 atm

Automatic sequential air sampler

GCxGC



Provided by Gerstel K.K.

Components are separated by 1 st GC, and the modulator leads all of the components to 2 nd GC column every 3 -8 seconds.

Result

	December 17-19, 2012				December 25-27, 2012			
	TD	R	HV	R	TD	R	HV	R
HCB	101	62	86	82	118	68	95	73
alpha-HCH	31	61	22	77	23	70	18	81
beta-HCH	5.1	67	1.8	79	4.4	66	2.3	75
gamma-HCH	11	66	7.3	75	8.9	65	6.4	69
trans-chlordane	26	82	34	91	22	78	28	87
cis-chlordane	15	–	17	–	13	–	21	–
trans-nonachlor	22	77	27	89	15	79	19	82

TD (pg/m^3) : TD+ GCxGC -MS/MS, 0.2L/min (0.86m^3)

HV (pg/m^3) : HV+ GC/HRMS, 250L/min (1,008m ^{3})

R (%) : surrogate recovery

Application

	TD-GCxGC-MS/MS	Data (Cape Hedo, 2009)			
	IDL (pg)	warm		cool	
		conc. (pg/m^3)	applicability	conc. (pg/m^3)	applicability
HCB	0.15	80	○	90	○
HCHs	0.08 – 0.27	0.1 – 11	○1)	0.1 – 14	○1)
Chlordanes	0.11 – 0.23	1.2 – 10	○	0.1 – 0.7	○2)
DDTs	0.05 – 0.25	0.15 – 3	○3)	0.1 – 2	△
Drins	0.12 – 0.43	0.05 – 2.2	△	ND – 0.5	×
Mirex	0.11	0.2	△	0.07	×

The applicability is based on the assumption of 1 m^3 collection for 3.5 d.

1) except delta -HCH
2) except cis-Nonachlor
3) except DDDs and *o,p'*-DDE

IV–2 <2012~2014>

Cooperative research on bioaccumulation on POPs and related chemicals

Japan - Noriyuki SUZUKI, Takeo SAKURAI
Korea - Igchun EOM, Byoungcheun LEE, Jisung RYU

1. Background

POPs and related chemicals show essentially multi-medium behavior in the environment. Therefore, estimation of their multi-medium behavior is an important topic of concern on the management of POPs in both of the countries. Based on this common understanding, cooperative researches on long-range-transport modeling and bioaccumulation of these compounds had been conducted.

Recently designated POPs and their related compounds (new POPs) include those show higher water solubility (e.g., PFOS) and those used in different applications, such as flame retardants in consumer products, than conventional POPs. The multi-medium behavior of these compounds, particularly that related with bioaccumulation is still to be elucidated.

This cooperative research focuses on the behavior of new POPs in the aquatic system, and modeling of bioaccumulation, and thus contribute to the development of modeling multi-medium behavior of these compounds, coupled with the achievements from the previous cooperative studies.

2. Research Plan

1) Information collection and experimental study that form the basis of behavior modeling of new POPs in the aquatic system by both countries.

2) Investigation and information sharing on the modeling of new POPs by both countries. Comparison and sharing of the results and the related information between the two countries.

3. Major Outcomes

The cooperative research conducted bioaccumulation modeling and laboratory studies of perfluorinated compounds (PFCs) and hexabromocyclododecane (HBCDs), investigated the essential processes of bioconcentration and bioaccumulation of these compounds, and was successful in sharing information and experiences of bioaccumulation studies of the recently designated POPs and their related compounds in the aquatic environment.

<KOREA>

1) In this study, BCF (L/kg), BAF (L/kg) and bioconcentration (ng/g) for PFCs (PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA and PFOS) were predicted using a modified bioaccumulation model and compared with measured data. The results showed that

BCFs, BAFs and bioconcentration values for PFCs in species of aquatic ecosystem were found to have higher values with the increase in chain length. When comparing predicted and measured data, the PFOA and PFDA showed a relatively good correlation. However, additional measured data are needed because its quantities are insufficient. Although further improvement is required, the model simulation can be used to estimate the level of ecosystem exposure at a screening level.

2) BCF, BAF and bioconcentration values for PFCs in six species of aquatic ecosystem were found to have higher values with the increase in tropical levels and PFCs chain length. When comparing predicted and measured data, the results were well-fitted, but additional measured data are required because its quantities are insufficient.

3) Previous studies reported that HBCD is bioaccumulative according to existing POPs screening criteria (BCF > 5000) and all isomers have estimated log Kow >5. However, no high accumulation of HBCD was observed in O. latipes.: The BCF value of HBCD in whole body was 96. This biomass was not sufficient to analyze uncertainty of treated water concentration, requiring dietary exposure method and more organisms. Further studies are needed to identify the bioaccumulation of HBCD based on the uncertainty of bio-isomerization and biotransformation rates for each isomer.

<JAPAN>

1) Marine fish are important as a food source, but chemical transfer studies therein have been limited. In this study, uptake kinetics, specifically uptake efficiency from the dissolved phase in marbled flounder were experimentally determined for PFOS. Uptake efficiency is an essential parameter regarding chemical uptake, but it has been reported in a limited number of studies. Our results not only contribute to the better accuracy of the prediction of chemical transfer to marine fish, but also indicate the necessity of further research in this area, particularly regarding the mechanisms of uptake of ionized chemical species.

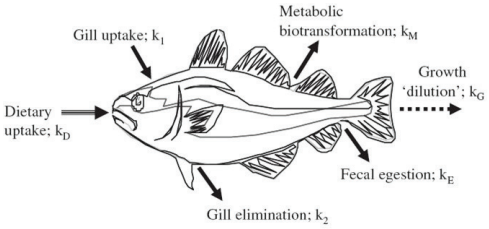
2) The basic formulation of a bioaccumulation model of PFOS in fish has been completed. Physiological parameters have been defined for PFOS and CB#138. Our future work will focus on the following aspects: (1) Modeling concentrations in food; (2) Dynamic solution; (3) Validation plan (field sampling); (4) Generalization and parameter estimation for other PFASs; and (5) Sensitivity/uncertainty analysis.

3) We advanced the bioaccumulation modeling of PFOS in a marine benthic fish. Our achievements are as follows: (1) PFOS concentrations in sandworm as a model prey species were modeled by an application of the basic model structure; (2) The model was demonstrated to predict concentrations dynamically with changes in environmental parameters, and; (3) Basic formulation of coupling organism energetics with PFOS kinetics was studied. This needs further study. Our future work aims to establish these models further, focusing on: (1) Energetics–kinetics coupling (continued); (2) Some technical aspects of dynamic solution; (3) Generalization and parameter estimation for other PFASs; (4) Sensitivity/uncertainty analysis; and (5) Validation plan and field sampling. These modeling efforts contribute to gaining better understanding of potential levels of PFOS and related compounds in fish.

Highlight Slides, KOREA

Japan-Korea Bilateral program meeting (21 Feb, 2013)

Aquatic bioaccumulation model & predicted BAF(L/kg) data



Species	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTeDA	PFOS
O. latipes	12	39	156	802	4500	16500	-	2700
R.oxycephalus	13	42	170	882	5100	19500	-	3000
C. carpio	16	51	212	12	9400	38600	-	4800
S. sjerzeri	17	55	230	1400	12900	63500	-	6200

BCF(Bioconcentration factor) = CB/CWD = k1/(k2+kE+kM+kG)
BAF(Bioaccumulation factor) = (k1+kD(CB/CWD)) /(k2+kE+kM+kG)
CB(Concentration in the organism) = (k1+kDΣPiCD,i)/(k2+kE+kM+kG)

Fig. 5 BAF model description and predicted data. This results was predicted to increase bioaccumulation as the number of carbon increase.

Japan-Korea Bilateral program meeting (21 Feb, 2013)

Bioaccumulation factor(BAF, L/kg); Predicted vs. Measured data

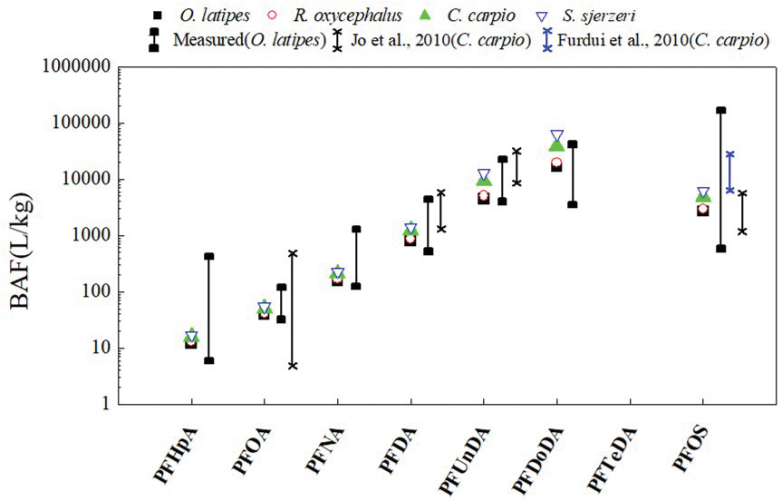
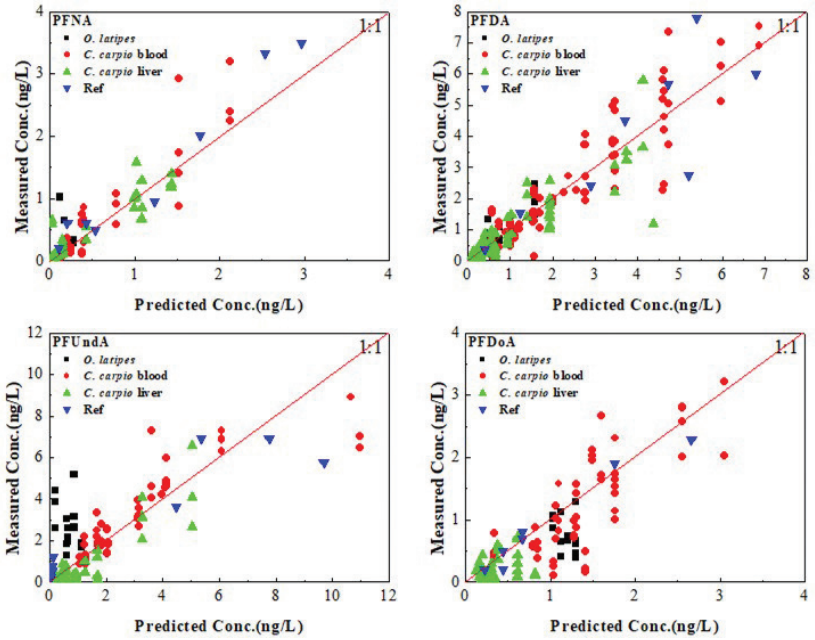


Fig. 6 Comparison of predicted and measured Bioaccumulation Factor values among aquatic organisms.

Korea-Japan Bilateral program meeting (6 Mar, 2014)

Bioconcentration(ng/g) predicted data vs measured data



Japan-Korea Bilateral program meeting (27 Feb, 2015)

Deca BDE transfer from aquatic environment of Crucian carp

- $BCF = C_f/C_w = K_1/K_2$

In this study	BCF (based on nominal conc.)
HBCD	96

- PBT and vPvB screening criteria according to European Commission TGD : BCF >2000 (PBT), 5000(vPvB)

BCF in literature studies

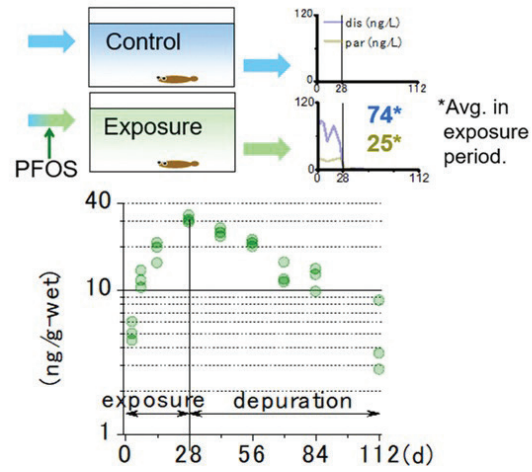
Species	isomers	Exposure condition	BCF	Reference
Fathead minnows *Pimephales promelas*	T-HBCD	32-day BCF test 6.2 µg/L	18,100	Veith et al. 1979
Rainbow trout *Oncorhynchus mykiss*	T-HBCD	35-day flow through bioconcentration test 0.34 and 3.4 µg/L (nominal) 0.18 and 1.8 µg/L (measured)	13,085 (High) 8,974 (Low)	Drottar and Krueger 2000
Rainbow trout *Oncorhynchus mykiss*	α, β, γ – HBCD	56-day (uptake), 112-day (depuration) Via diet separate aquaria for each diasteromer : Dietary Exposure method : Revised TG 305 at 2012	(Daetry) BMF α–HBCD : 9.32 B–HBCD : 4.3 γ –HBCD : 7.2	Law et al., 2006

Highlight Slides, JAPAN

Japan-Korea Bilateral program meeting (21 Feb, 2013)

Fish respiratory uptake efficiency of PFOS

- PFOS concentrations in fish increased in the exposure period, and then decreased in the depuration period.



Time course of PFOS concentration in fish (control < 0.06 ng/g-wet) (Sakurai et al., submitted)

Mass-specific oxygen demand (Marbled flounder, avg. 31 g, at 17.4 deg C)

3.1 mg-O_2/(g-wet d)

(Kobayashi et al., submitted)

Japan-Korea Bilateral program meeting (21 Feb, 2013)

Fish respiratory uptake efficiency of PFOS

- Uptake efficiency of PFOS was lower than that of neutral hydrophobic compounds.
  - Note: Some other ionizing compounds show higher uptake efficiency.

	PFOS, marbled flounder (*1*)	PFOS, other fish (*1–5*)[a)]	PCBs & Pesticides[b)], marbled flounder (*6*)
Uptake efficiency	**1.8%**[d)]	0.6%–7%[c)]	16%–150% [median, 84%][d)]
Half-life (d)	**33**	13–110	2.7–220~

a) Whole-body results were compared.

b) log K_{OW} > 3.7.

c) Calculated by using oxygen uptake efficiency of the Japanese flounder (0.53).

d) We re-analyzed the literature data.

(1) Sakurai et al., submitted; (2) CERI, 2001; (3) 3M, 2003; (4) Martin et al., 2003a, 2003b; (5) Ankley et al., 2004 (6) Kobayashi et al., submitted.

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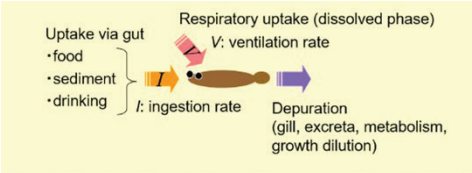
Korea-Japan Bilateral program meeting (6 Mar, 2014)

Model prediction and uptake routes



$$\frac{dC_b}{dt} = \frac{V}{M}\alpha_r C_{dis} + \sum_i \left(\frac{I_{(i)}}{M}\alpha_{g(i)} C_{f(i)}\right) - k_d C_b$$

	C_{dis} (ng/L)	C_{sed} (ng/g-dry)	$C_{b\text{-model}}$ (ng/g-wet)	r_{dis}	r_{food}	$C_{b\text{-field}}$ (ng/g-wet)
PFOS	2.3[a]	0.61[a]	3.6	66%	34%	34[b]
CB#138	0.0025[c]	1.2[c]	56	<0.1%	>99.9%	0.31–1.2[d]

a Sakurai et al. (2010); b Taniyasu et al. (2003) [converted to wet basis by using Sakurai et al. (2013)]; c Kobayashi et al., 2010; d Kobayashi et al., unpublished data.

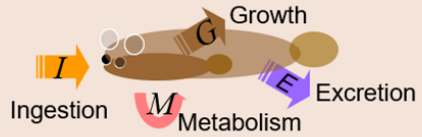
- Model assumptions
  - C_b at steady state, $C_b(0) = 0$.
  - Fish mass constant (M = 157 g-wet, 2-y old [Kume et al., 2006]).
  - Same conc. in food items as in sediment on an organic-matter basis.
- Major uptake route differs between PFOS and CB#138
- Different sampling times and high estimated conc. in food may have resulted in gaps between modeled and field-obs. conc.

Japan-Korea Bilateral program meeting (27 Feb, 2015)

Coupling energetics with PFOS kinetics: Feasibility

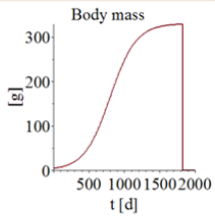
Energy budget

$$I = M + G + E$$



Feasibility run

Growth:



Metabolism: $M = 6.75W^{0.784}$ [mg-O_2/d]

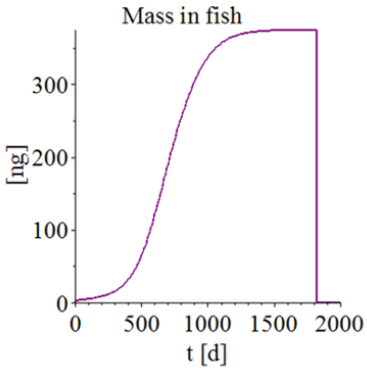
[Sakurai et al. 2013]

Ingestion: $I = (M + G)/a$

a: food assimilation. efficiency. (0.7)

[Fonds et al. 1992]

Depuration: $b_d = f(W)$



- PFOS bioaccumulation described in relation to fish physiology.

IV-3 <2012~2014>

Comparison of the amount of perfluoroalkyl substances (PFASs) accumulation in freshwater fish (Crucian carp) and the surrounding environmental media between Korea and Japan

Korea - Giho JEONG, Byoungcheun LEE, Jisung RYU, Jeongeun OH
Japan - Kiwao KADOKAMI, Hanako SHIRASAKA, Rento HIDAKA

1. Background

Per- and polyfluoroalkyl substances (PFASs) are considered eternal chemicals because they are difficult to degrade, and their regulation is being considered by the Stockholm Convention. In this study, we investigated the concentration levels of PFASs accumulated in fresh water fish (crucian carp) inhabiting major rivers in Japan and Korea, and compared the accumulation levels of PFASs in both countries in the same way as we have done for POPs such as dioxins and OCPs. In addition, we measured PFASs concentrations in sediments and clarified correlations with accumulation levels in fish. By examining this, we will conduct comparative studies and harmonize monitoring methods between both countries regarding the pollution status of river ecosystems and the assessment of bioaccumulation of PFASs.

2. Research Plan

1) To investigate accumulation levels of perfluoroalkyl substances (PFASs) in crucian carp.

2) PFASs, including 3-5 types of PFSAs (perfluorosulfonic acids) and 9-11 types of PFCAs (perfluoroalkyl carboxylic acids), were selected as analysis target materials.

3) To identify differences in accumulation levels between sampling sites and both countries and to elucidate the causes.

4) To improve analysis technology level through analysis technology exchange between Korea and Japan.

3. Major Outcomes

<KOREA>

1) Carp muscle: The total concentration of PFCs was in the range of 0.57 - 43 ng/g wet wt. Isomers with relatively short carbon chains were not detected at any point or were detected only at one or two points, while isomers with long carbon chains were detected at almost points. The concentration range of PFCs (unit: ng/g wet wt.): carboxylic acids PFHxA <0.01 (=MDL) - 0.58, PFOA <0.04 - 0.12, PFNA <0.09 - 0.36, PFDA 0.06 - 2.4, PFUnDA Below the detection limit of <0.05 - 1.3, PFDoDA <0.03 - 1.0, PFTrDA <0.04 - 0.54 and PFTeDA <0.02 - 0.40, PFHpA <0.06; For sulfonic acids, PFHxS was 0.11 in only one individual, PFOS was 0.15

- 17, and PFDS was <0.06 – 0.32.

2) PFCAs were distributed approximately twice as much as PFASs, and in particular, PFOS is overwhelmingly abundant. However, in sediments, no one isomer accounts for a particularly high proportion. In sediments, PFCAs and PFASs were distributed at a much higher at a ratio of 1:4, whereas in fish samples, the ratio was almost 2:1 in both muscles and eggs. The average detected concentration was 0.15 for sediment, 7.7 for muscle, and 86 ng/g (wet wt) for egg.

3) The distribution ratio of long-chain isomers (C9 to C14) increases in the following order: sediments (63%), crucian carp muscle (73%), and crucian carp egg (93%), As a result of investigating the correlation between the length and weight of crucian carp, it was found that there was a significant correlation coefficient of 0.9065 between the length and weight of a total of 48 crucian carp.

<JAPAN>

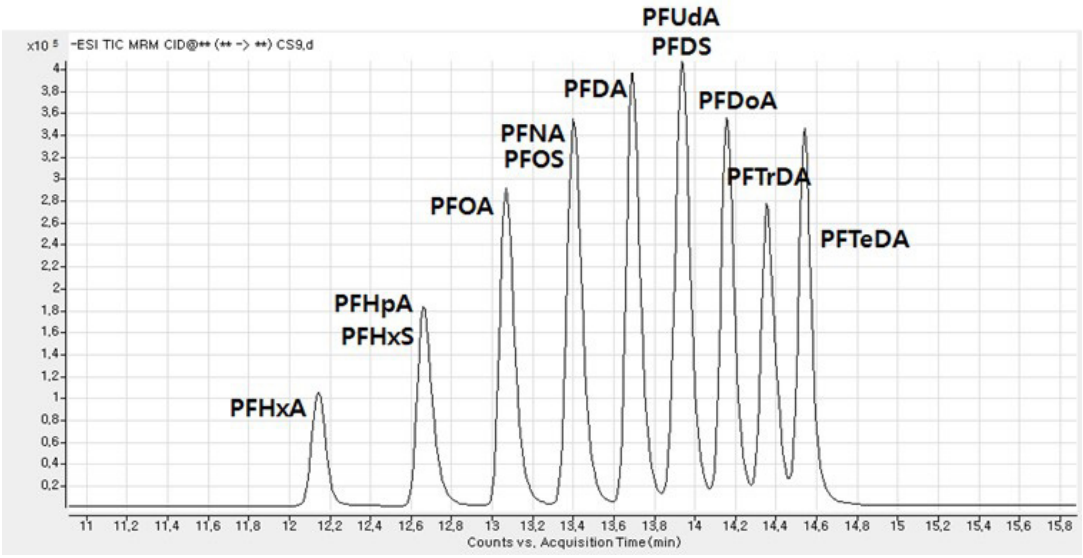
1) The average concentrations of 14 perfluorosulfonic acid (PFSAs) and 5 perfluoroalkyl carboxylic acids (PFCAs) in crucian carp collected in 2003 were 3.46 ng/g (0.166 - 17.5) and 5.53 ng/g (1.28 - 12.7), respectively. PFASs were detected in high concentrations in large cities, but concentrations in remote areas were much lower than in other regions. Perfluorooctane sulfonates (PFOS) and PFCAs with longer chains (>10) were predominant in the fish.

2) Concentrations of PFASs in tissues differed, with the liver having the highest concentration (33.6 ng/g wet), followed by eggs (17.2), others (15.5) and muscle (9.4). The maternal transfer rate of PFASs was 19%, similar to those of legacy POPs. Concentrations of PFASs in fish appeared to be proportional to body weight, with concentrations increasing as body weight increased, indicating that accumulation levels in fish increase with age. Bioconcentration ratios of PFASs (ratio of concentrations in the body to those in water) ranged from thousands to tens of thousands, indicating that PFASs are easily bioaccumulated.

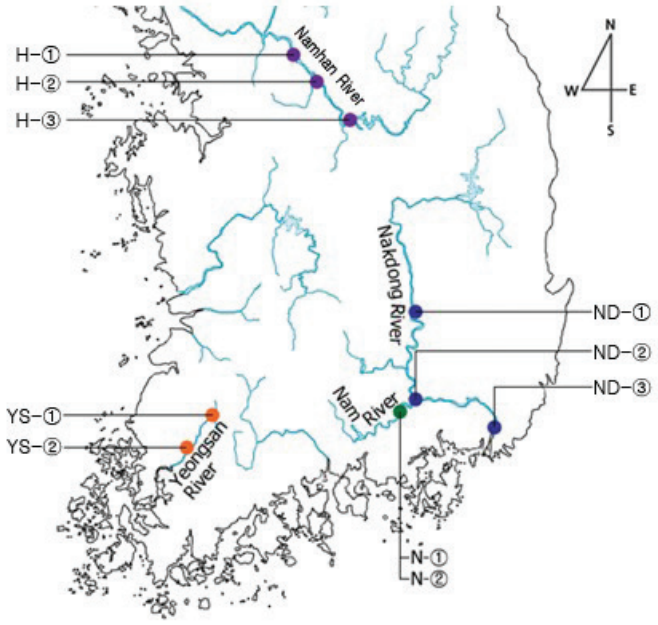
3) Concentrations of PFASs in 2014 were lower than in 2003: the arithmetic mean concentration of PFASs in fish at the five sites in 2014 was 8.90 ng/g wet and the geometric mean concentration was 6.25 ng/g wet, which were lower than those before the POPs Convention regulation (2003) (13.96 ng/g wet and 10.36 ng/g wet) .

Highlight Slides, KOREA

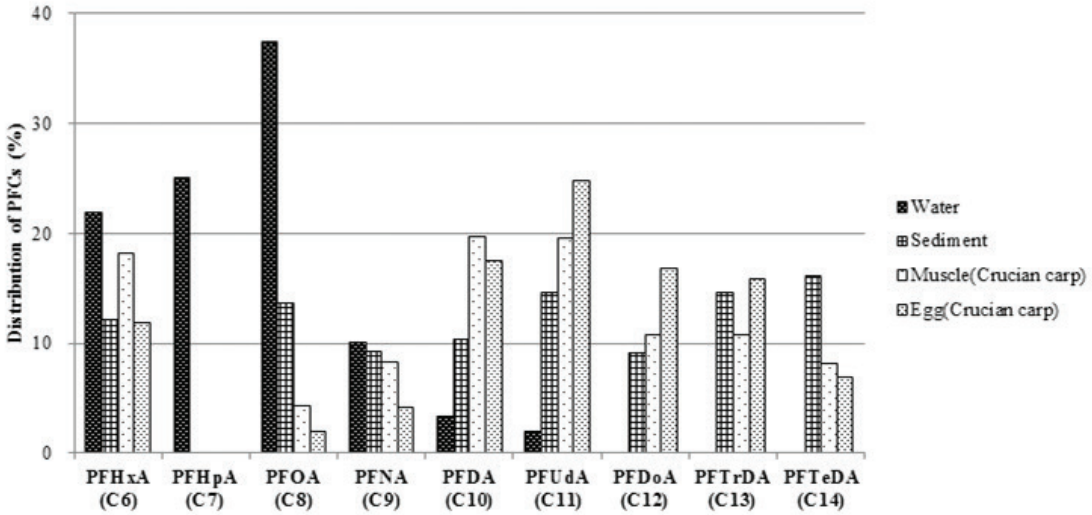
LC-MS/MS standard chromatogram of perfluorinated compounds



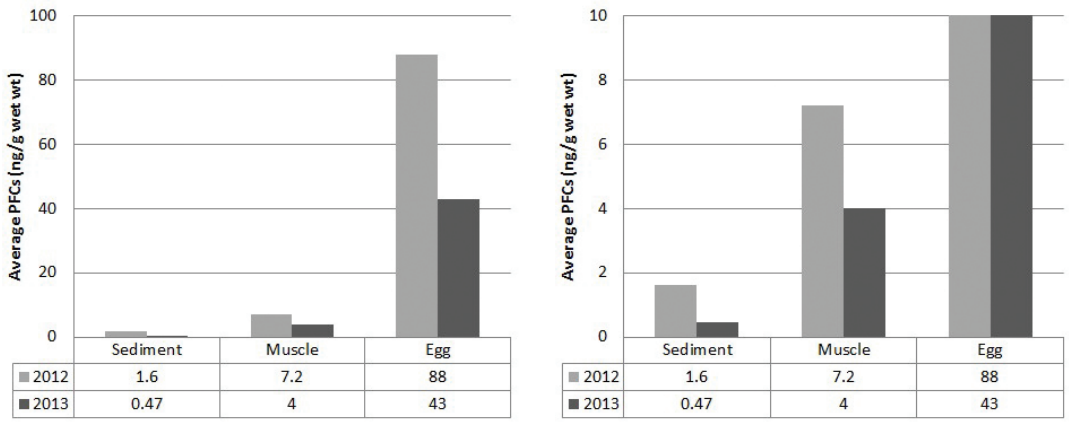
Sampling sites, Korea

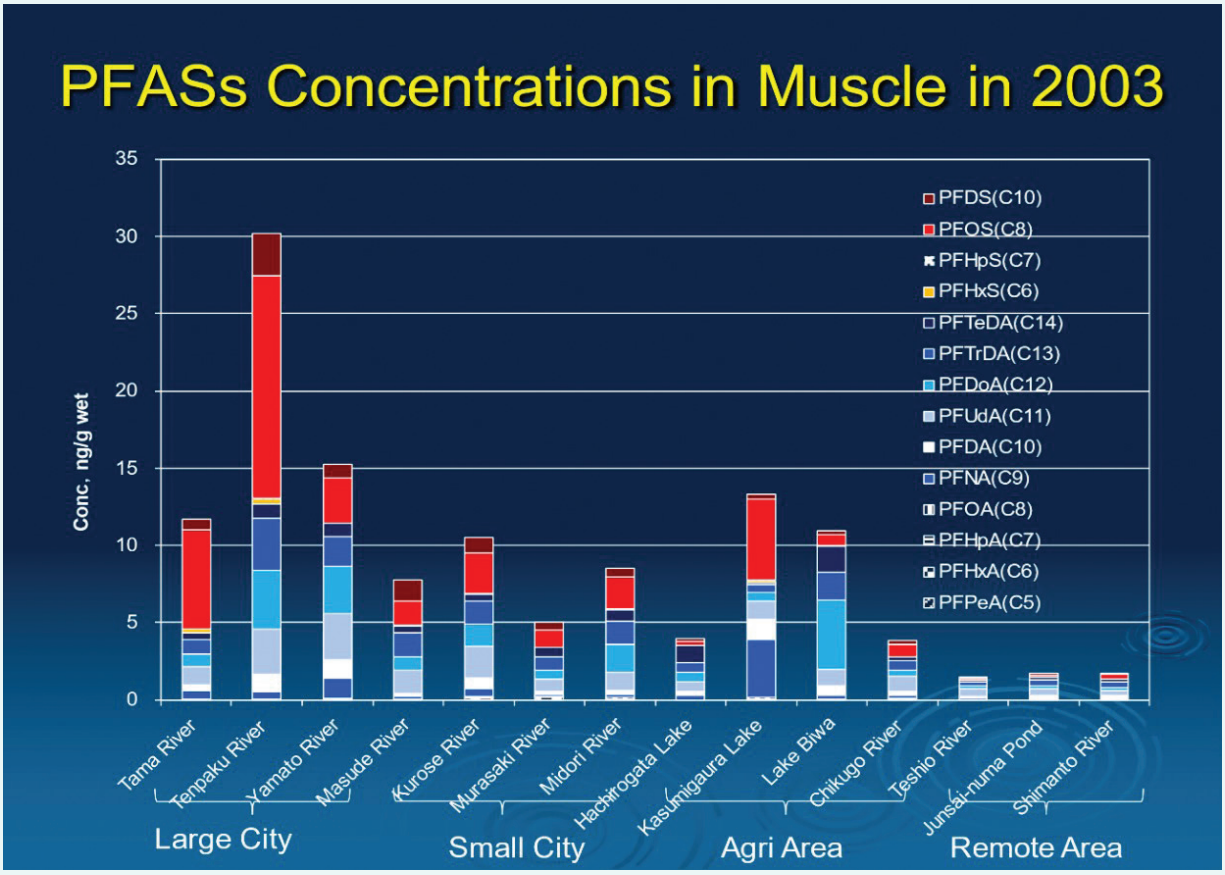


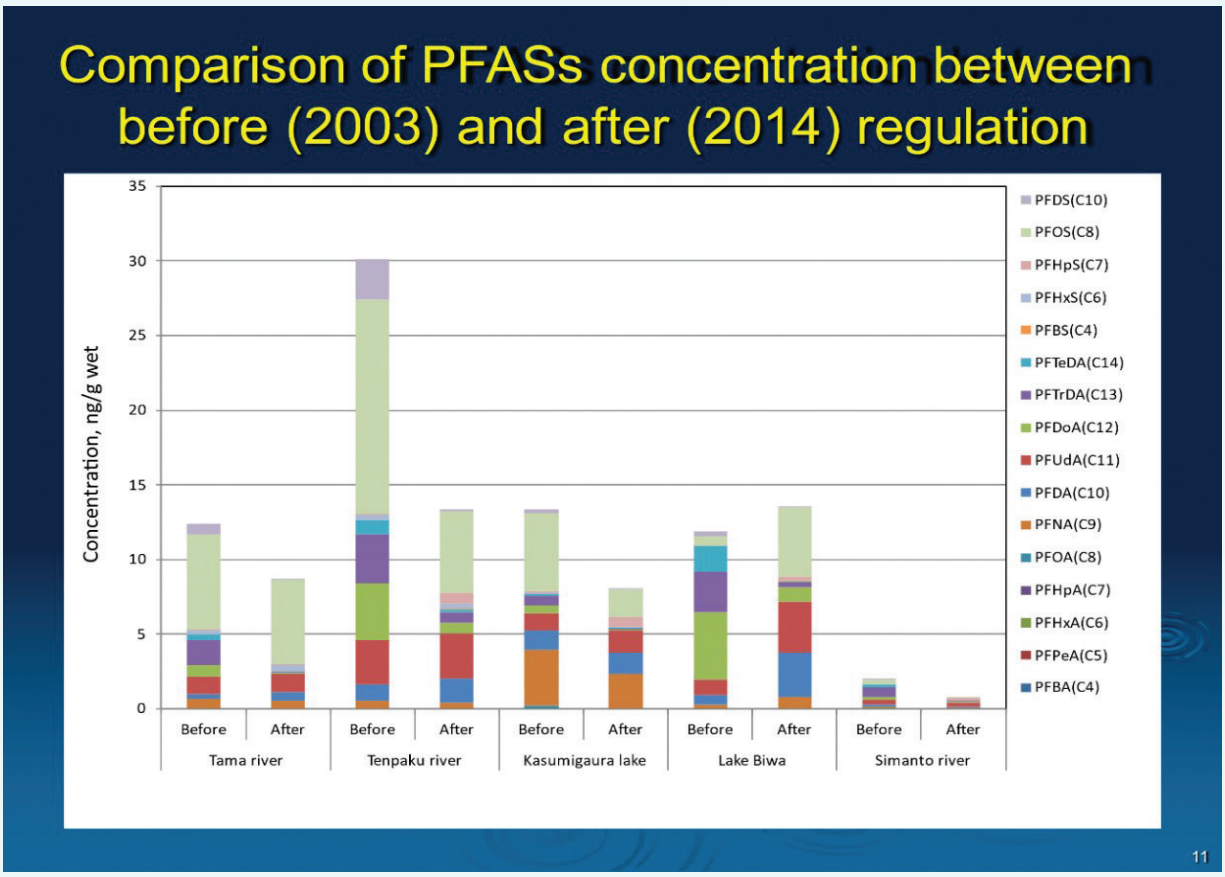
Distribution of PFCAs homologs according to carbon chain length



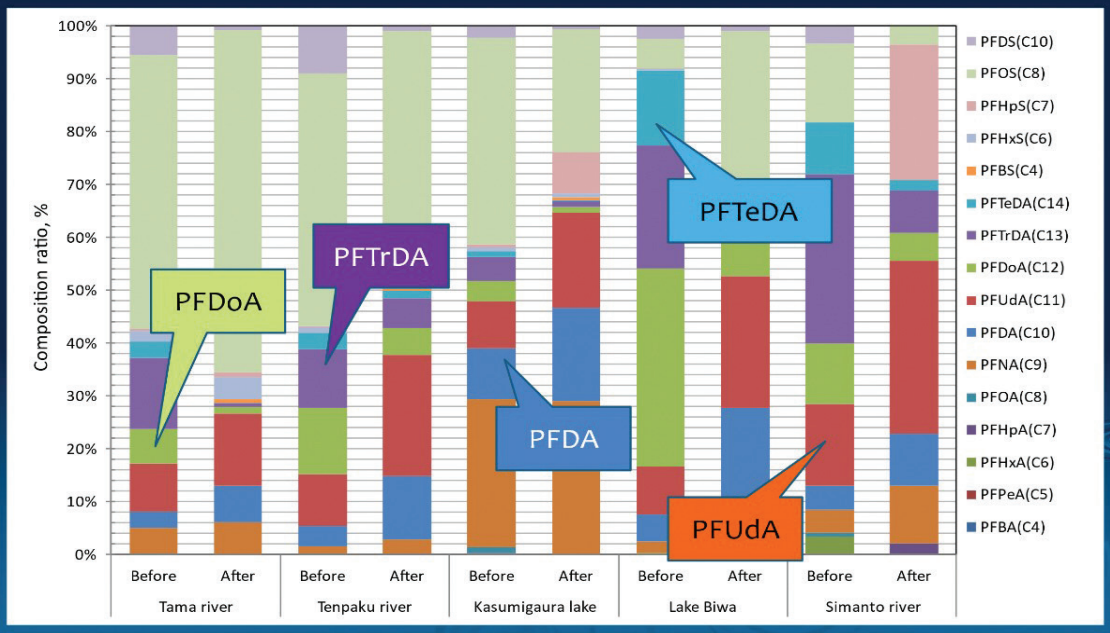
Comparison of perfluorinated compound concentration (ng/g wet wt.; 2012, 2013)




PFASs Concentrations in Muscle in 2003
Conc, ng/g wet
35
30
25
20
15
10
5
0
PFDS(C10)
PFOS(C8)
PFHpS(C7)
PFHxS(C6)
PFTeDA(C14)
PFTrDA(C13)
PFDoA(C12)
PFUdA(C11)
PFDA(C10)
PFNA(C9)
PFOA(C8)
PFHpA(C7)
PFHxA(C6)
PFPeA(C5)
Tama River
Tenpaku River
Yamato River
Masude River
Kurose River
Murasaki River
Midori River
Hachirogata Lake
Kasumigaura Lake
Lake Biwa
Chikugo River
Teshio River
Junsai-numa Pond
Shimanto River
Large City
Small City
Agri Area
Remote Area

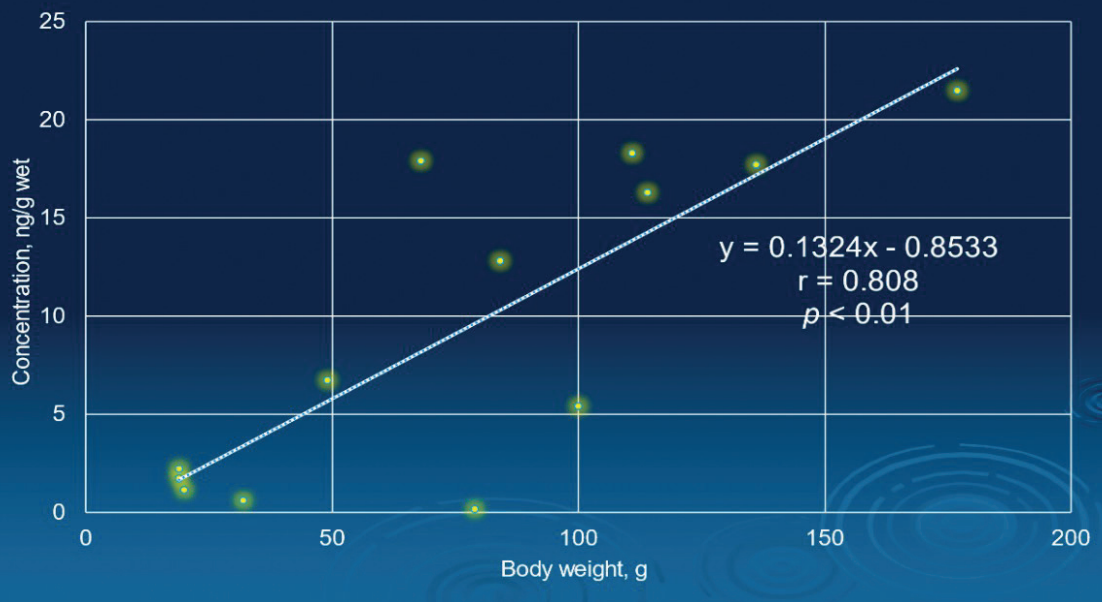

Comparison of PFASs concentration between before (2003) and after (2014) regulation
Concentration, ng/g wet
35
30
25
20
15
10
5
0
PFDS(C10)
PFOS(C8)
PFHpS(C7)
PFHxS(C6)
PFBS(C4)
PFTeDA(C14)
PFTrDA(C13)
PFDoA(C12)
PFUdA(C11)
PFDA(C10)
PFNA(C9)
PFOA(C8)
PFHpA(C7)
PFHxA(C6)
PFPeA(C5)
PFBA(C4)
Before
After
Tama river
Tenpaku river
Kasumigaura lake
Lake Biwa
Simanto river
11

Comparison of PFASs profile between before and after regulation in Japan



12

Relationship between PFASs Concentration and Body Weight



14

IV-4 <2012~2014>

Comparison of monitoring results and toxicological data for perfluorinated chemicals between Japan and Korea

Japan – Norihisa TATARAZAKO, Norimistu SAITO, Kazuaki SASAKI, Katsumi IWABUCHI, Masafumi ONO
Korea - Igchun EOM, Junheon YOON, Jaean LEE, Byoungcheun LEE, Hyeonseo CHO, Kyunghwa PARK, Jisung RYU

1. Background

Perfluorinated chemicals such as PFOS and PFOA are persistent in the environment and have been shown to bioconcentrate in aquatic organisms. In fact, these have been detected not only in sediment downstream of a sewage plants but in the river water by our studies. We have already developed the technique that can measure PFOS from one medaka. Therefore, Korea and Japan must cooperate to investigate quantity of PFOS/PFOA in several medium (soil, water, sediment and biota) in detail. Now, we harmonized a measuring method between the two countries and laid the situation which could communalize the measurement data.

On the other hand, the results of medaka which we carried out last year in a laboratory confirmed that PFOS accumulated in the body of the medaka, but showed that the toxicity was not high in the short term exposure. However, we performed multi-generations exposure study in the low-dose / long term under the situation that is close to the environment to clarify ecological adverse effects of PFCs.

With monitoring results in several medium from both countries and relevant toxicity data, the risk assessment of the perfluorinated chemicals will be performed.

2. Research Plan

The research cooperation between Korea and Japan will include the followings

1) Environmental monitoring data in stream water, sediment and medaka will be collected in Korea and Japan to clarify the expansion of PFOS/PFOA in the environment.

2) Investigate the low dose/long term exposure study of new POPs.

3) Brush up monitoring technique and harmonize it between Korea and Japan.

3. Major Outcomes

1) Analytical method of PFOS/PFOA was harmonized between the two countries. Therefore, the result of a measurement of the two countries can be compared in the same point of view in the future. The PFOS and PFNA concentration that accumulated in one Medaka could be measured by improving our microanalysis technology. Then, the relation between toxicity and accumulation of PFOS/PFOA in Medaka was clarified.

2) In Korea, PFOS concentration in river water of medaka habitat: Gimhae > Hadong > Yeosu > Sacheon > Gwangyang

PFCs in medaka body: high concentration of PFOS, PFUnDA, PFDA

High concentrations of PFOS and PFOA were detected in surface water of surveyed rivers affected by national wastewater and sewage treatment plants.

PFCs in crucian carp blood: high concentrations of PFOS, PFDA and PFUnDA; high contaminating levels of PFCs in Nakdong river and Yeongsan river.

PFCs in crucian carp liver: PFOS was highest concentration PFC; high contaminating levels of PFCs in Yeongsan river.

PFCs concentration in carp blood: relatively higher than in carp liver

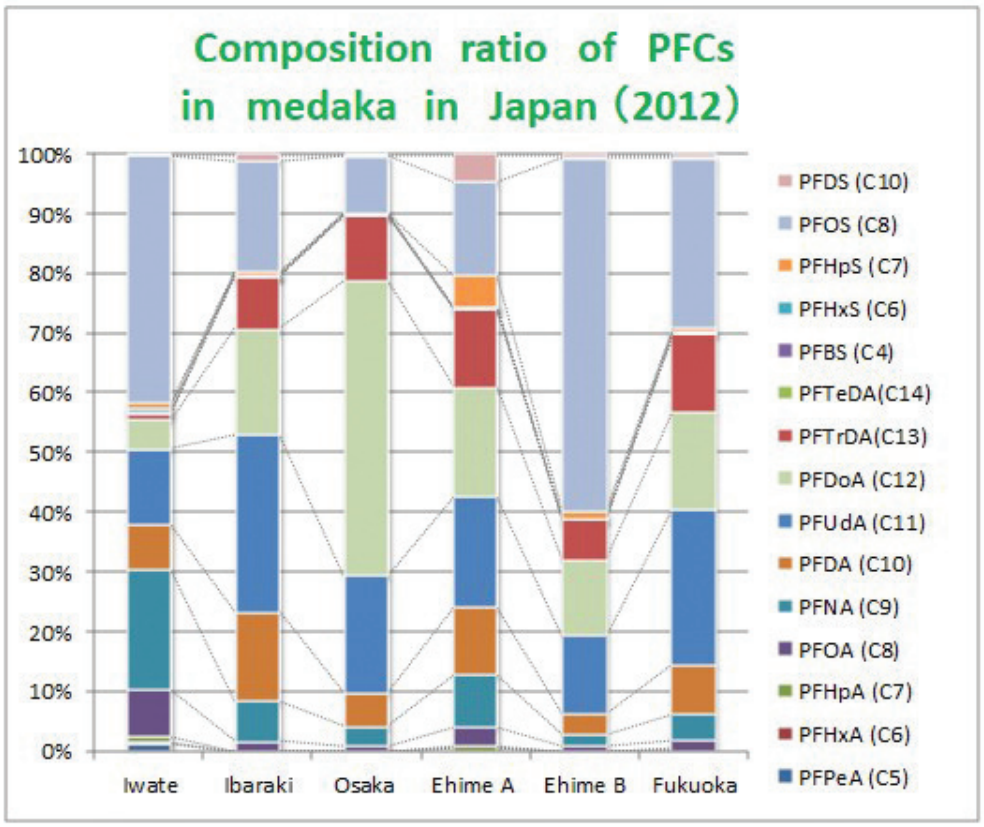
Detected PFCs concentration: water < sediment < Carp liver < medaka < Carp blood

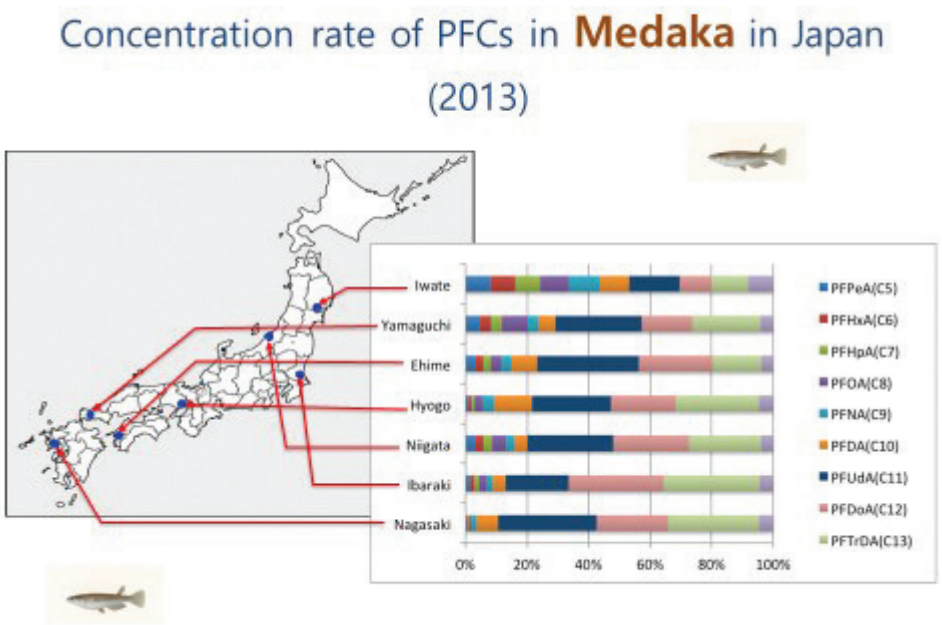
High BCF in carp blood and liver and medaka fish: PFDA and PFUnDA

3) Comparative Conclusion in medaka habitat

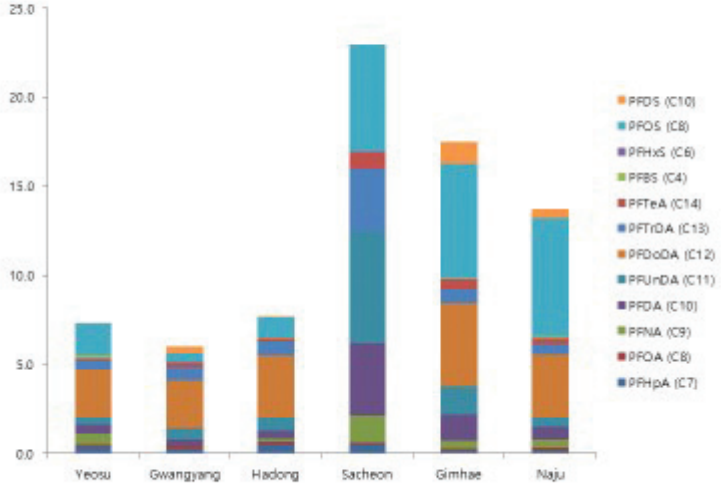
- Japan: PFCs concentration in river water was 0.1-70 ng/L
  PFOA > PFNA, PFHpA, PFHxA, PFOS >> PFBS, PFHxS
- Korea: PFCs concentration in river water was 1.6-11.6 ng/L
  PFOA > PFNA, PFDA, PFHxA, PFOS >> PFBS, PFHxS
- Japan: PFCs concentration in sediment was 0.13-1.8 ng/g-dry
  PFDoA > PFUdA > PFDA > PFNA
  PFOS
- Korea: PFCs concentration in sediment was 0.3-0.4 ng/g-wet
  PFDoA > PFUdA > PFOA > PFDA
  PFOS
- Japan: PFCs concentration in medaka was 3-69 ng/g
  PFOS >> PFDS
  PFDoA > PFUdA > PFDA > PFNA
- PFCs concentration rate (medaka/river water = y)
  PFCAs y = 0.8237e1.181x R^2 = 0.9402
  PFSAs y = 19.1e0.8965x R^2 = 0.8032
  x: carbon number (4–14)

Highlight Slides, JAPAN/KOREA

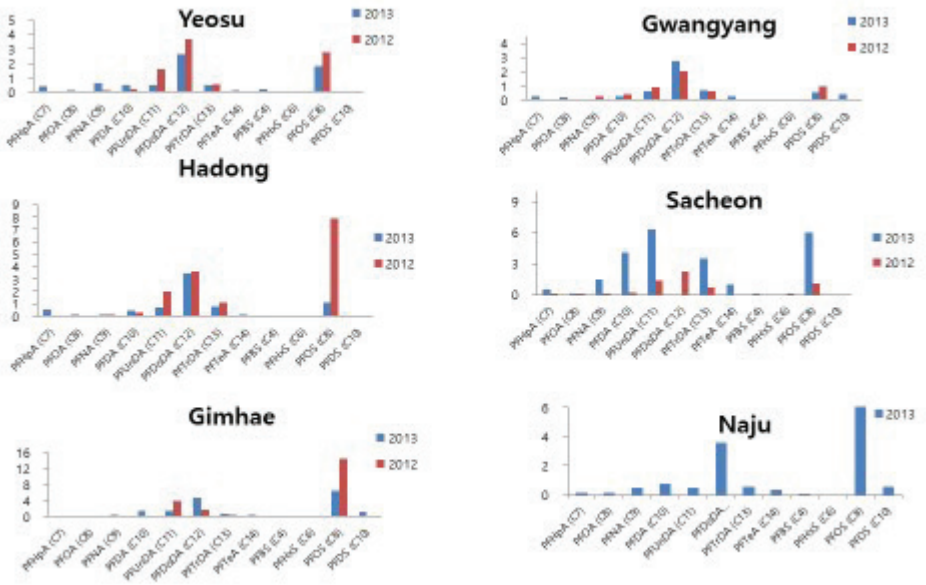




Mean PFCs concentration in medaka wholebody



Medaka wholebody concentration (ng/g wet wt) comparisons



Concentration of PFCs in **Environmental Water** in Japan (2014)

10

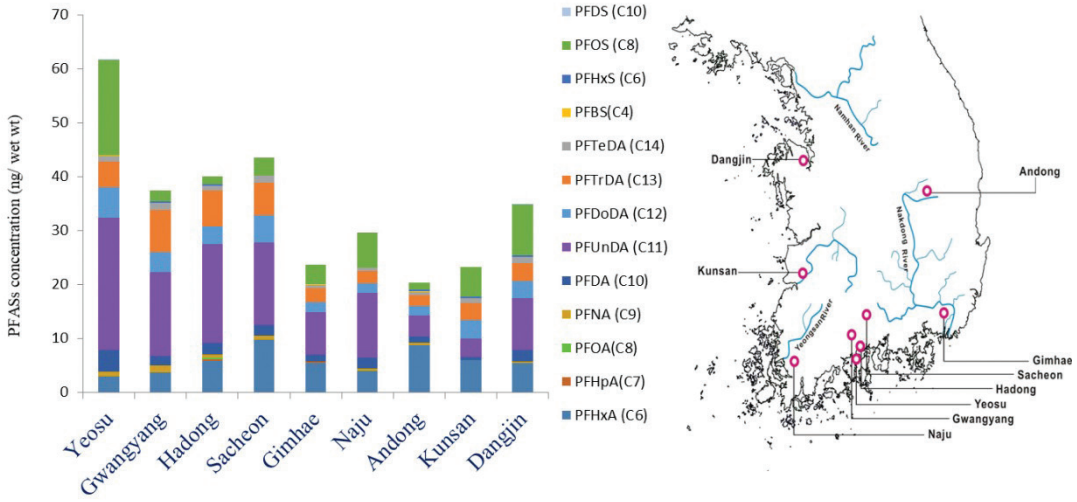
Concentration of PFCs in **Sediment** in Japan (2014)

11

Concentration of PFCs in **Medaka** and **Kadayashi(Mosquitofish)** in Japan (2014)

13

MEAN PFASS CONCENTRATION IN MEDAKA WHOLEBODY



3.3 Changing Period of CJR (2013-2022)

V-1 <2015~2017>

Mercury isotope analysis as a new tool to support Minamata Convention on Mercury

Korea - Minseob KIM, Jongwoo CHOI, Jaeseon PARK, Jeeyoung KIM
Japan - Akinori TAKEUCHI, Akane YAMAKAWA, Yasuyuki SHIBATA

1. Background

As international interest in mercury (Hg) pollution increases, the 5th Intergovernmental Negotiating Committee (INC5) held in Geneva on January 19, 2013 agreed to adopt the Minamata Convention, and 50 countries ratified it on May 18, 2017. In accordance with the provisions of the agreement, it officially came into effect on August 16, 2017, 90 days later. The Minamata Convention is the world's first agreement to manage the production, storage, use, discharge, and disposal of a single chemical substance to reduce environmental hazards caused by Hg. It also includes Hg supply and trade, Hg -added products, and air quality. Main contents such as water and soil discharge, storage and disposal are covered. Among environmental pollutants, Hg, known as the cause of Minamata disease in Japan, is a transition metal element on the periodic table that exists in a silver-colored liquid state at room temperature. The existence of Hg has been well known since ancient times, and it has been widely used to extract gold from mines.

In the natural environment, changes in chemical species occur through various reactions such as microbial decomposition, abiotic reactions, and photochemical reactions, and it is known that mobility varies greatly depending on the chemical species. In particular, methylmercury accumulates easily in living organisms and is highly toxic, so various studies are being conducted on it. Recently, Hg stable isotope ratio research has been conducted to track Hg pollution sources. Hg has 7 stable isotopes, and the average abundance in nature is ^{196}Hg (0.15%), ^{198}Hg (9.97%), ^{199}Hg (16.87%), ^{200}Hg (23.10%), ^{201}Hg (13.18%), ^{202}Hg (29.86%), and ^{204}Hg (6.87%). Hg stable isotope ratio is analyzed using Multi-collector Inductively Coupled Plasma Mass Spectrometry (MC/ICP/MS) equipment, and a linked device is used to Wet Plasma, Dry Plasma, Cold Vapor Generation (CVG), and Gas Chromatograph-MC/ICP/MS that simultaneously analyzes organic Hg and inorganic Hg.

2. Research Plan

1) NIES, Japan, will analyze Hg isotope ratios of certified reference materials (CRMs) and natural samples in order to reveal global and regional scale environmental cycling of Hg as well as to reveal major sources of Hg to human beings. A remote rake, Lake Mashu, will be selected as representative field study.

2) NIER, the Republic of Korea, has been focusing on Hg isotope signature as a new scientific tool for environmental forensic studies and will continue a measure the CRMs to improve Hg analytical methods. Harmonization of the method including Quality Assurance (QA)/Quality Control (QC) procedure will be jointly conducted.

3. Major Outcomes

<KOREA>

1) The cooperative project has been conducted for developing Hg isotope analytical methods and applying them to reveal sources and environmental behavior of Hg.

2) In NIER, in order to harmonize the pre-treatment and analysis procedure for Hg isotope analysis of human hair samples (NIER-13 CRM), 2 researchers visited NIES in last year.

3) In recently, NIER conducted collection efficiency of Hg isotope in ambient air samples through carbon trap (TGM) and Ontario hydro (GOM, GEM) method. Additionally, NIER measured Hg isotope compositions of sediments to reveal sources of Hg.

<JAPAN>

1) Hg isotope analytical methods were intercalibrated between NIER and NIES, and transformation and fate of Hg in the Lake Mashu ecosystem were investigated.

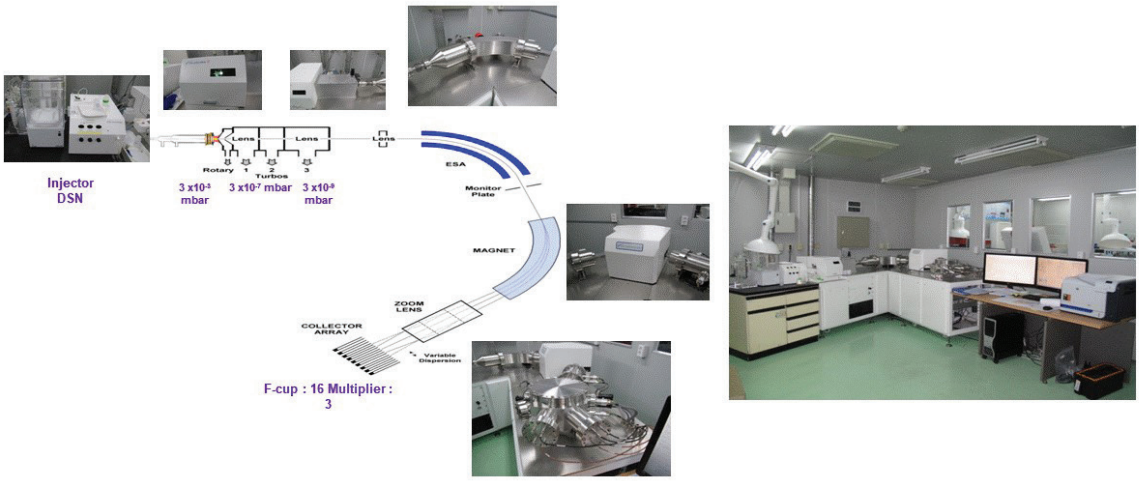
2) The determined Hg isotope compositions of the CRMs at NIES were similar to the previously documented values, and Hg isotope lab at NIES can generate the precise and accurate Hg isotope values.

3) Hg isotope variations in the Lake Mashu fish and sediment indicated that Hg in the sediments could be a source of methyl-Hg. Hg isotope variations in fish also indicated a different degree of photoreduction prior to entering each MeHg bioaccumulating pathway.

4) This study suggested that Hg isotope analysis could track the transformation and fate of Hg in the terrestrial aquatic environment.

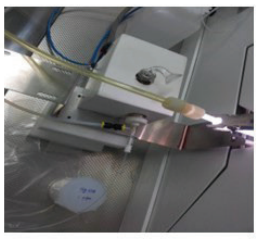
Instrument use for Hg analysis

Multiple Collector- Inductively Coupled Plasma-Mass Spectrometer



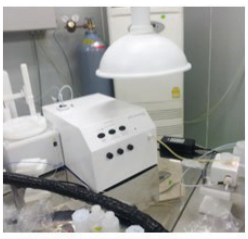
Introduction systems of MC/ICP/MS
for heavy metals and inorganic Hg analysis

Wet Plasma



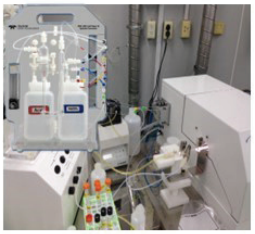
- Direct injection to plasma
- Easy to use
- But, High LOD

Dry Plasma



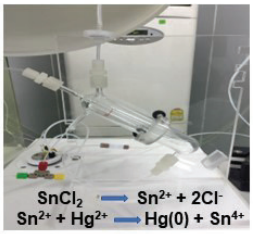
- By using membrane nebulizer
- Accuracy & Precision → 10 X
- Small amount sample

Cold Vapor Generator



- Accuracy & Precision → high
- Low LOD
- But, Large amount sample

Gas-Liquid Separator



- Accuracy & Precision → high
- Low LOD
- Small amount sample

1

Harmonization between NIER and NIES

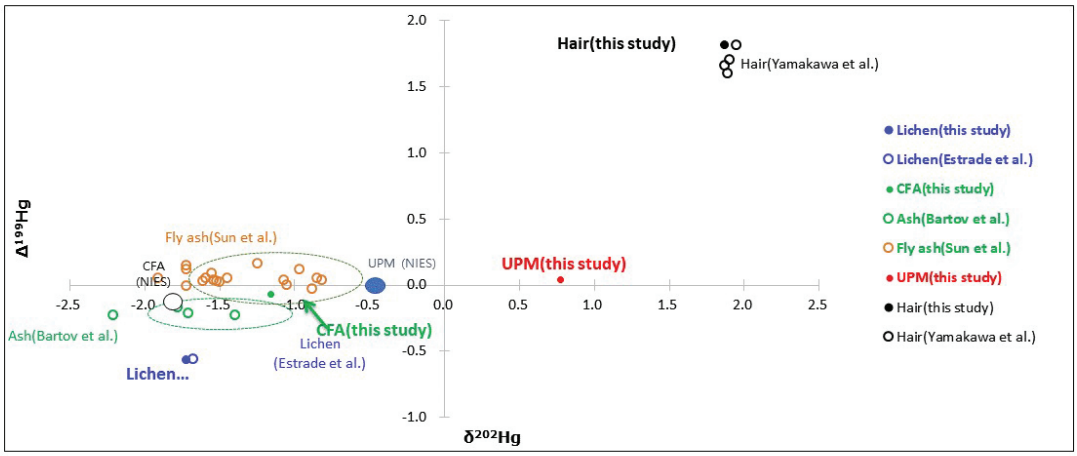
- Hg Isotope analysis and pretreatment of environmental CRMs (Lichen, Coal Fly Ash, Urban Particulate Matter, Hair) in NIES

  ※ (2016. 03. 15 ~ 18. , 2017. 12. 18 ~ 20, NIER scientists visited in NIES)



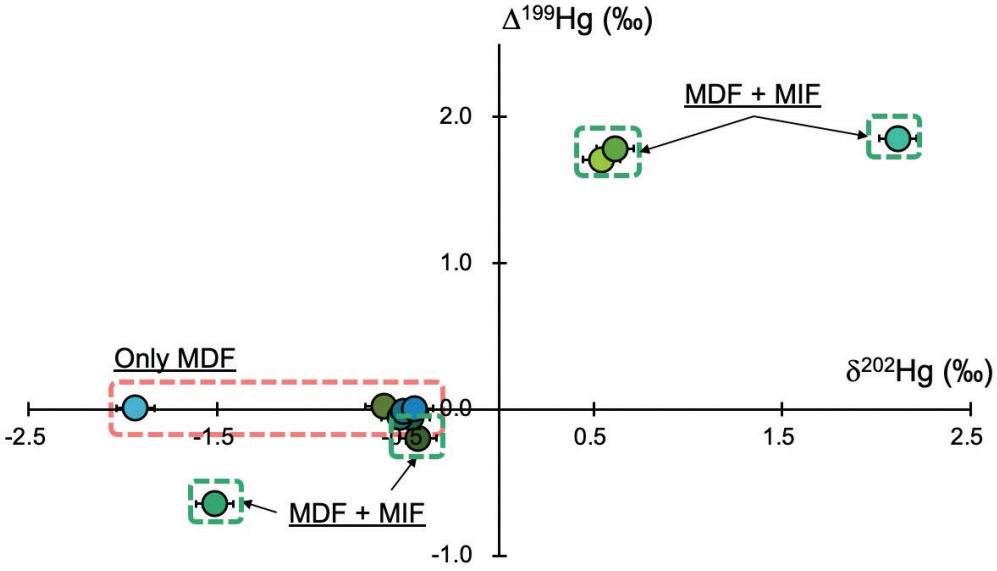
Mercury isotope composition in Environmental CRM

✓ Results of Mercury stable isotopic ratio in Environmental CRMs

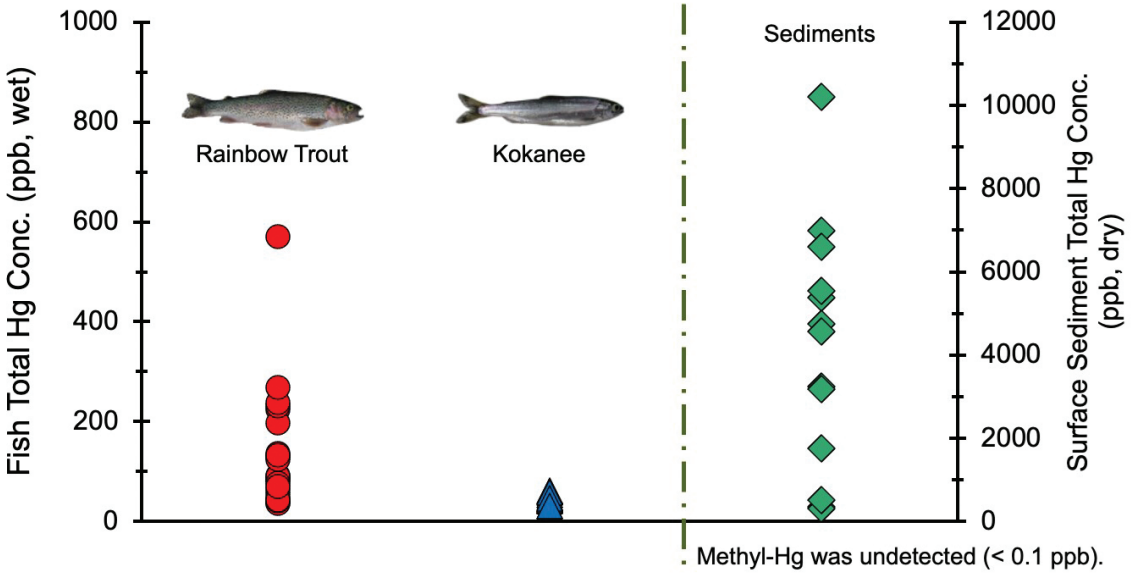


- Lichen – BCR 482, Coal Fly Ash (CFA) – NIST 1633c, Urban Particulate Matter (UPM) - NIST1648a in this study

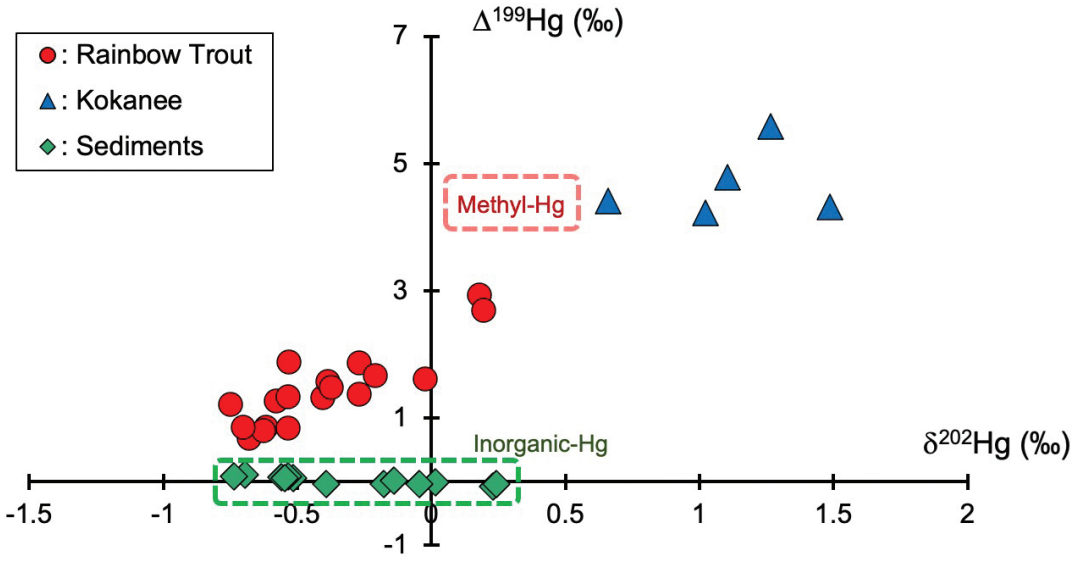
Results of the Hg Isotope Compositions of the Samples Prepared by NIER (NIES's Results)



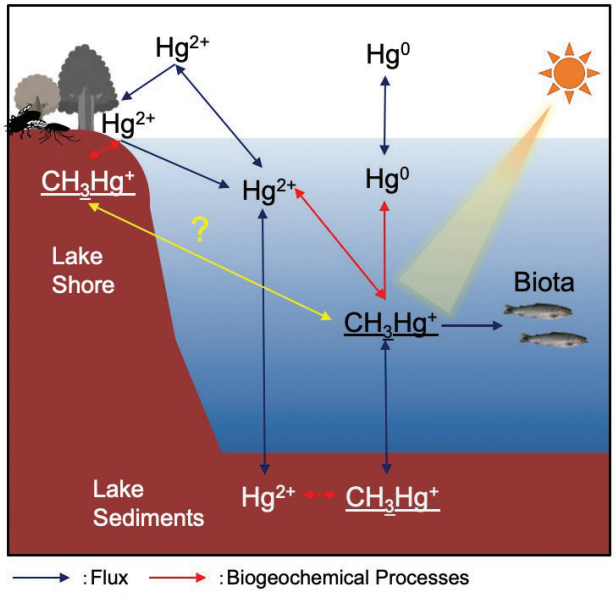
Lake Fish & Surface Sediment Hg Concentrations



Hg Isotope Compositions (Fish & Sediments)



Lake Mashu Hg Biogeochemistry & Summary



1. Sources of Methyl-Hg

Hg isotope variations in fish and sediment indicate that Hg in the sediments can be a source of methyl-Hg.

Hg isotope variations in fish indicate a different degree of photoreduction prior to entering each MeHg bioaccumulating pathway

Plant litterfall can be another source of methyl-Hg from terrestrial environment based upon the relatively high Hg concentration.

2. Natural Tracer of Hg

Hg isotope analysis can track the transformation (i.e., Redox Reaction & Methylation) and fate of Hg in the environment.

V–2 (2015~2017)

Cooperative research on bioaccumulation of emerging contaminants in fishes

Japan - Noriyuki SUZUKI, Takeo SAKURAI, Norihisa TATARAZAKO
Korea - Jeongeun OH, Kyunghwa PARK, Jisung RYU, Jaewoo LEE, Byoungcheun LEE, Hyeonseo CHO

1. Background

POPs and related chemicals exhibit essentially multi-medium behavior in the environment. Therefore, the estimation of their multi-medium behavior is an important topic of concern for the management of POPs and other related chemicals in both countries. Based on this common understanding, cooperative research on long-range-transport modeling and bioaccumulation of these compounds has been conducted, including those with higher water solubility and various emission sources.

This cooperative research will focuses on the behavior of new POPs and other emerging contaminants in the aquatic system, clarifies details of bioaccumulation properties, through experimental, field-study, and modeling approaches, and thus contribute to the development of models for multi-medium behavior of these compounds.

2. Research Plan

1) The hexabromocyclododecanes (HBCDs) which serve as substitutes for PBDEs were designated as POPs under the Stockholm Convention in 2013 and some of the perfluoroalkyl acids (PFAAs) are currently under review for inclusion as POPs in addition to PFOS which was listed in 2009.

2) Additionally, the polychlorinated naphthalenes (PCNs) were recently designated as persistent organic pollutants (POPs) under the Stockholm Convention.

3) A limited number of studies on these new and candidate POPs has been conducted to investigate their occurrence, distribution, and bioaccumulation in the environment in comparison to conventional POPs. It is essential to understand the occurrence and fates of these emerging POPs in the environment.

4) The Korean researchers will study bioaccumulation of polychlorinated naphthalenes (PCNs) and hexabromocyclododecanes (HBCDs) in the aquatic environment using field monitoring data.

5) The Japanese researchers will study bioaccumulation of perfluoroalkyl acids by means of either experimental, field-observation, or modeling method.

3. Major Outcomes

<KOREA>

1) The analytical method for HBCDs in various environmental samples comprising fish,

water and sediment was developed, and the monitoring and bioaccumulation of HBCDs in Korean aquatic environment were conducted for two years.

2) Additionally, the analytical method for PCNs in various environmental samples comprising fish, water and sediment was developed, and the bioaccumulation of PCNs in Korean aquatic environment was examined by analyzing PCNs in fish, river water and sediment samples.

<JAPAN>

1) The bioconcentration of PFAAs in medaka (*Oryzias latipes*) was modeled by using a physiologically-based mass-balance based model, and the model predictions were compared with field observations. Respiratory transfer kinetics of perfluorooctanesulfonate (PFOS) in a marine sandworm species was investigated by a laboratory experimental study.

2) Also, the bioaccumulation of PFAAs in an estuarine food-web in Japan was modeled. Model parameters of uptake and depuration kinetics were examined, and the model predictions were compared with field observations.

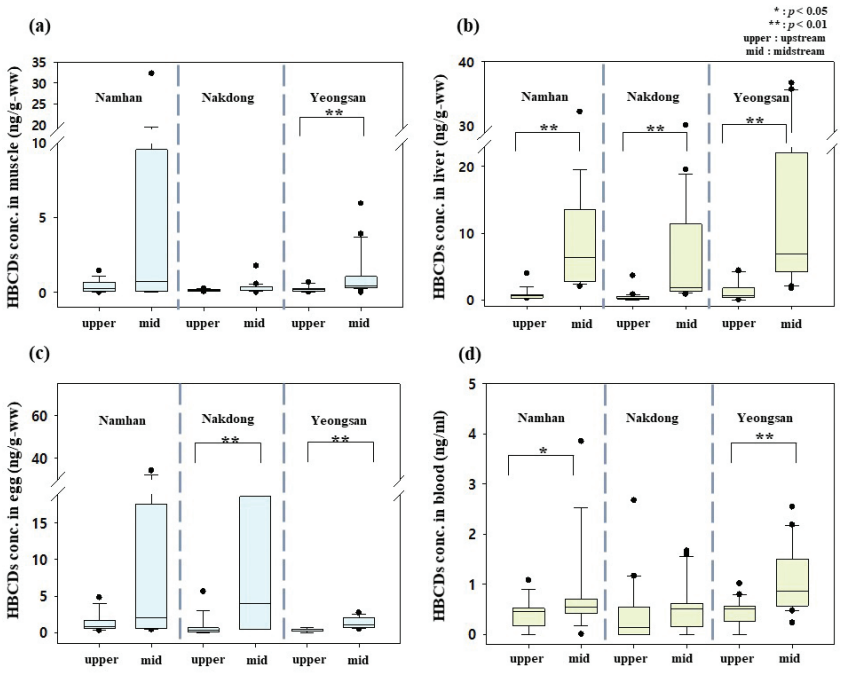


Figure. Hexabromocyclododecane (HBCD) concentrations in crucian carp tissues (ng/g-ww.), (a) muscle, (b) liver, (c) eggs, and (d) blood (ng/ml), showing statistically significant differences between upstream and midstream sections of three major Korean rivers.

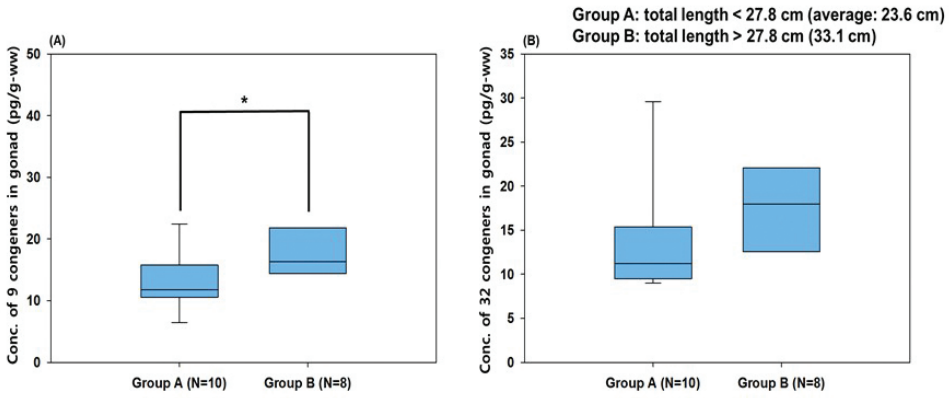


Figure. The relationship between PCN accumulation in crucian carp gonads and total length; (A) concentrations of nine PCN congeners in gonads versus total length, (B) concentrations of 32 remaining PCN congeners (previous nine congeners excluded) in gonads versus total length.

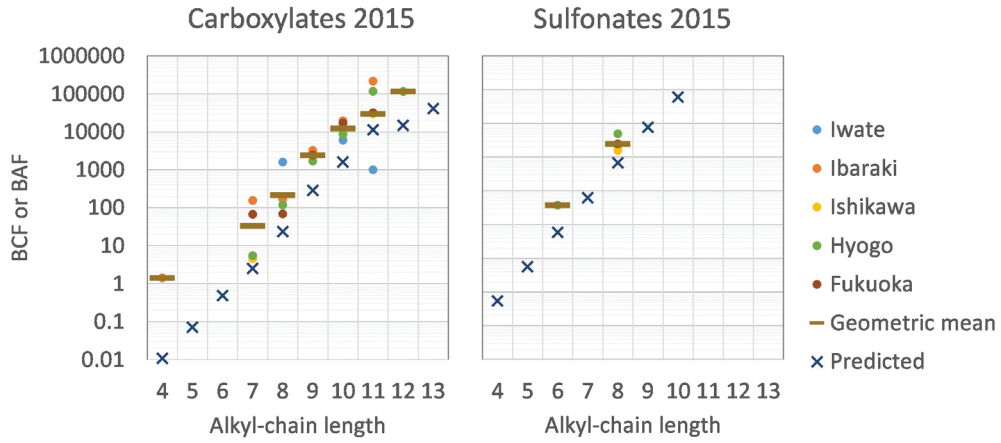
Table Average values of the biota–sediment accumulation factor (BSAF) and the bioconcentration factor (BCF) of hexabromocyclododecanes (HBCDs) in crucian carp tissues, along with a comparison to the results of previous studies

	Compound	Species	Muscle	Liver	Egg	Blood	Reference
BSAF	**HBCDs**	**Crucian carp**	**1.11 0.14 [N]***	**25.6**	**11.6**	**2.83**	**This study**
	HBCDs	benthic invertebrates	0.45				van Beusekom et al., 2006
		Common bleak	0.1–1.44				
	PAHs	Various fishes	0.1×10^{-5} – 0.8				van der Oost et al., 2003
	PCDD		0.1×10^{-2} – 0.13				
	OCPs		3–42				
	PCBs		1–37				
BCF (L/kg)	**HBCDs**	**Crucian carp**	**1,504 137,000 [N]**	**19,357**	**19,119**	**2,413**	**This study**
	PFOS	Crucian carp	-	4,572	-	11,167	Lam et al., 2014
	HBCDs	Fathead minnow	18,100				Veith et al., 1979
		Rainbow trout	19,200				Drottar et al., 2000
	PCDD/F	Common carp/Big head	109,648–104,472,855				Wu et al., 2001
	Endrin	Yellow tetra fish	6,200				Jonsson et al., 1993
	Dieldrin		2,384				
	4-MBC	Roach	9,700–23,000				Balmer et al., 2005

*[N] = Lipid content (%) and total organic carbon (%) normalized value.

Results

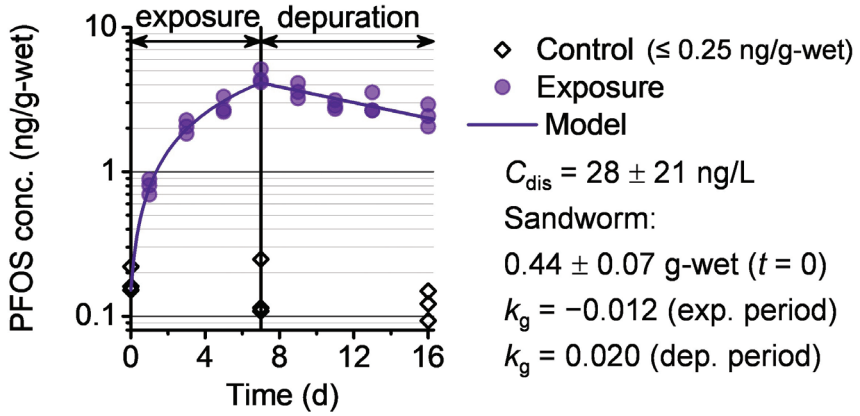
- Model predictions generally followed the observed trend with alkyl chain length and difference between sulfonates and carboxylates.
- Model underpredicted observed BAFs, particularly for the shorter chain compounds.



11

Slide presented at the 15th Joint Symposium on POPs Research (4 March 2016)

The kinetic model was successfully fitted to the data[1)]



Parameter	Value	95% CI	Unit
r	1.5	[0.89–2.1]	mg-O_2 g-wet^{-1} d^{-1}
k_{resp}	22	[7.9–70]	mL g-wet^{-1} d^{-1}
α^*_{PFOS}	11%	[3.9%–30%]	
$t_{1/2}$	15	[10–26]	d
BCF (k_{resp}/[k_e+k_m])	470		mL g-wet^{-1}

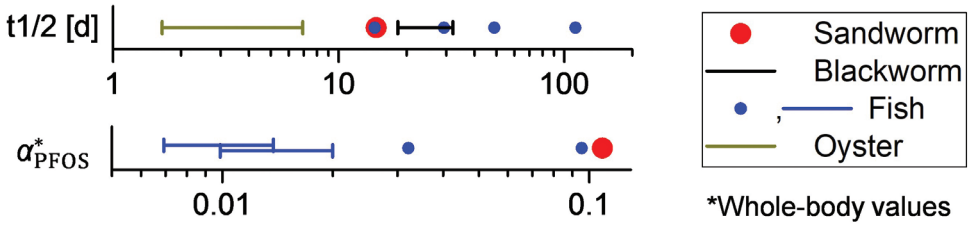
1) Sakurai T et al. (in preparation);

25

Slide presented at the 16th Joint Symposium on POPs Research (22 February 2017)

Comparison with (re-analysis of) previous reports

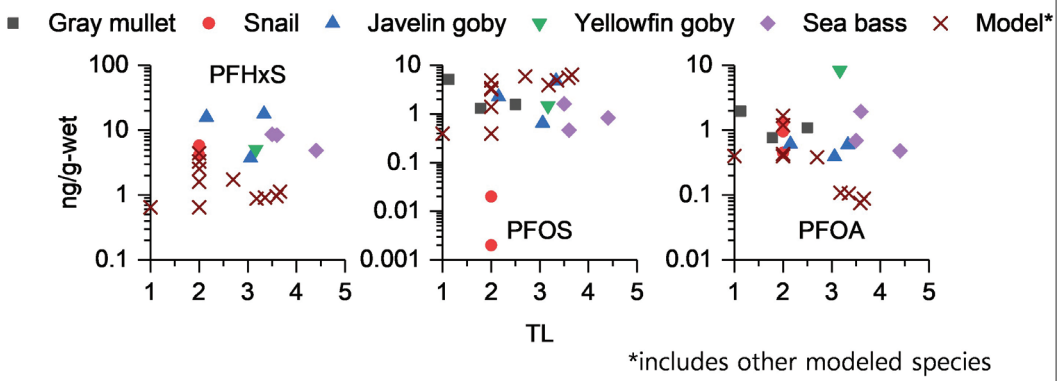
- Depuration half-life was comparable to or shorter than values* reported for a oligochaete[1)] and several fish species[2–6)].
  - Longer than that for oyster.
- Respiratory absorption efficiency (α^*_{PFOS}) was generally higher than the range of estimates* for the fish[2–11)].
  - Much lower than those typically reported for neutral hydrophobic compounds in fish (abs. value, 16%–150% [median 84%])[8,12)].



1) Higgins CP et al. 2007; 2) Sakurai T et al. 2013; 3) Martin JW et al. 2003; 4) CERI. 2001; 5) Inoue Y et al. 2012; 6) 3M, 2003; 7) Jeon J et al. 2010; 8) Kobayashi J et al. 2013; 9) Ankley GT et al. 2004; 10) Yamamoto K et al. 1988; 11) Winberg GG. 1956; 12) McKim J et al. 1985.

Slide presented at the 16th Joint Symposium on POPs Research (22 February 2017)

PFAA concentration and trophic level (TL)



- ❖ Observed concentrations of most compounds showed flat or slightly decreasing trends with TL
- ❖ The model generally reproduced these trends with TL
  - Note that higher TL organisms do not directly feed on lower TL organisms in this sample set

V–3 <2015~2017>

Cooperative research on environmental monitoring of POPs and other priority pollutants

Korea - Hyuk KIM, Yumi PARK, Inyoung CHUNG, Kyunghee CHOI
Japan - Yoshikatsu TAKAZAWA, Yasuyuki SHIBATA

1. Background

Article 16 of the Stockholm Convention requires the Parties to conduct environmental monitoring of priority media including air and submit "comparable" monitoring data to the Convention for the effectiveness evaluation. In East Asian countries, air POPs monitoring program and POPs training workshop have been conducted to support the Convention, and a new GEF project on POPs/new POPs analysis will start soon. In addition to the original 12 POPs, however, 14 new POPs have been added to the Convention and several candidates are under reviewed, and development and harmonization of POPs/new POPs monitoring methods are needed. Japan and the Republic of Korea have been conducting harmonization and development of POPs monitoring methods in this bilateral project and will continue the project for supporting sustainable environmental monitoring program.

2. Research Plan

1) NIES, Japan, will continue application of automated air sampling system in order to expand its performance for POPs and other priority pollutants.

2) NIER, the Republic of Korea, will conduct development of analytical method for new POPs, likely pentachlorophenol (PCP) and its salts and esters, hexachlorobutadiene (HCBD) and other priority pollutants in the environment.

3) Analytical methods of PCP and HCBD will be shared in both countries.

3. Major Outcomes

<KOREA>

1) NIER, the Republic of Korea, will conduct development of analytical method for new POPs, likely hexabromocyclododecane (HBCD) and other priority pollutants in the environment (2016)

2) NIER, the Republic of Korea, will conduct development of analytical method for new POPs, likely pentachlorophenol (PCP) and its salts and esters, hexachlorobutadiene (HCBD) and other priority pollutants in the environment (2017)

<JAPAN>

1) HCBD ranged from 880 to 1,200 pg/m^3 in Japan, and the concentration was high among airborne POPs.

2) The results of NIES observations over five months, showed no seasonal variation in HCBD concentration. This result may reflect the long half-life of HCBD e.g., 840 days in the Northern Hemisphere in the ambient air.

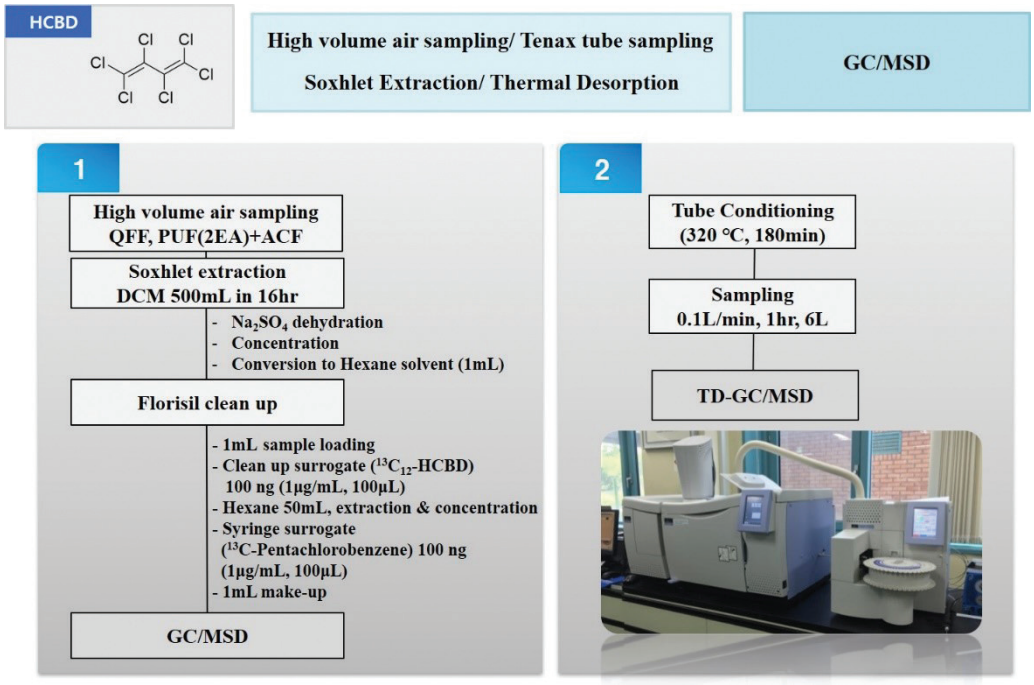
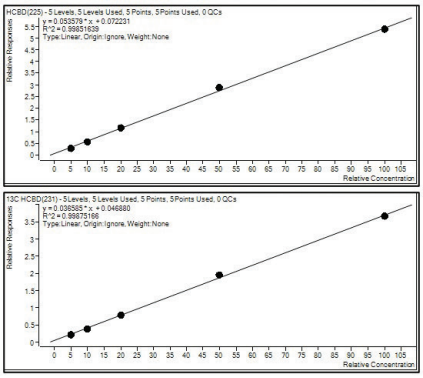


Fig. 1. Analytical flow charts of hexachlorobutadiene (HCBD) in air sample

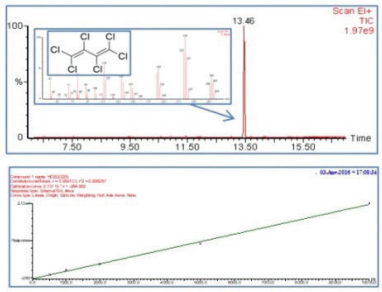


Standard range : 5~100ng/mL, $R^2 \geq 0.99$

GC	Instrument	Agilent Technologies 7890B
	Column	DB-VRX (60 m * 0.25 mm * 1.4 μm)
	Oven Temp.	120℃ (4.5 min) → 20℃/min to 210℃(0min) → 5℃/min to 240℃(8min) (Total times 23 min)
	Carrier gas	Helium (1.0 mL/min)
	Injector	250 ℃
	Transfer line temp.	230 ℃
	Injection volume	1 μL
	Injection mode	Split(2:1)
MS	Instrument	Agilent Technologies 5977A
	Ion source temp.	230 ℃
	Ionization	EI (Electron ionization)
	Measuring	SIM (Selected ion monitoring)

Compound		Quantification ion (m/z)	Identification ion (m/z)
Native STD	HCBD	225	260
Clean-up(Surrogate) STD	$^{13}C_4$ HCBD	229	264
Internal STD	$^{13}C_6$ Pentachlorobenzene	256	258

Fig. 2. Instrumental conditions HCBD analysis using high volume air sampler



Standard range : 0.5~10ng, $R^2 \geq 0.99$

TD	Instrument	PerkinElmer TurboMatrix 650
	Sample sweep mode Time	1min
	Sample Trap desorb	45mL/min for 1min at 310°C
	Sample Trap deseorb tube Temp.	-30°C
	Cryo trap desorb	10mL/min for 10min at 325°C
	Ratio	10 : 1
	Valve oven	200°C
	Transfer Line Temp.	200°C
	Flow	1.0mL/min
GC	Instrument	PerkinElmer Clarus 680
	Capillary column	DB-624 (60 m * 0.25 mm * 1.4 μm)
	Oven temp.	120°C (4.5 min) → 20°C/min to 220°C → 3°C/min to 240°C(1.32min) (Total times 16.99 min)
	Carrier gas	Helium (1.0 mL/min)
	Transfer line temp.	230 °C
MS	Instrument	PerkinElmer Clarus 600T
	MS source temp.	230 °C
	Ionization	EI (Electron ionization)
	Measuring	SIM (Selected ion monitoring)

Fig. 3. Instrumental conditions HCBD analysis using Tenax tube

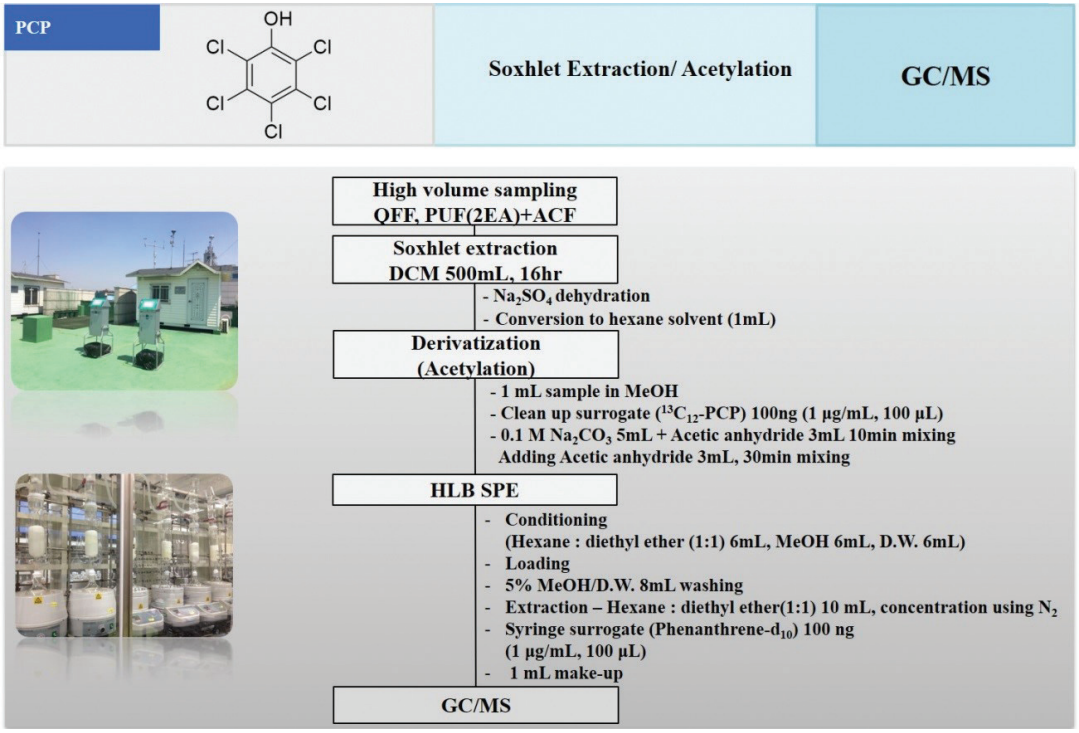


Fig. 4. Analytical flow charts of pentachlorophenol in air sample

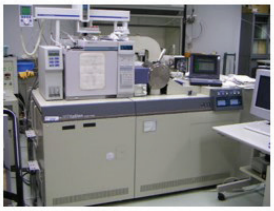
Air sampling (Tenax TA)

0.1L/min for 24h

Thermal desorption

^{13}C-PeCB: 100pg

GC/HRMS



GC	Instrument	Gerstel TDU + Agilent Technologies 7890A
	Column	DB-5MS (30m * 0.25mm * 0.25μm)
	Oven Temp.	50°C (0min) → 5°C/min to 130°C(0min) → 20°C/min to 200°C (25min)
	Carrier gas	Helium (1.0mL/min)
	Cold trap	Tenax TA, -10°C to 280°C
	Transfer line temp.	280°C
	Injection mode	Thermal desorption
	Desorption temp.	250°C
	Desorption flow	50mL/min
	Desorption time	10min
	Collection tube	6mm (O.D.), 60mm (length)
MS	Instrument	JEOL JMS-700K
	Ion source temp.	280°C
	Ionization Voltage	35V, EI (Electron ionization)
	Measuring	SIM (Selected ion monitoring)

13C HCBD recovery (%)
January 15-16, 2018 (HV sampling in NIES, 700L/min, 24h, 1000m³)
13C HCBD: 10,000 pg