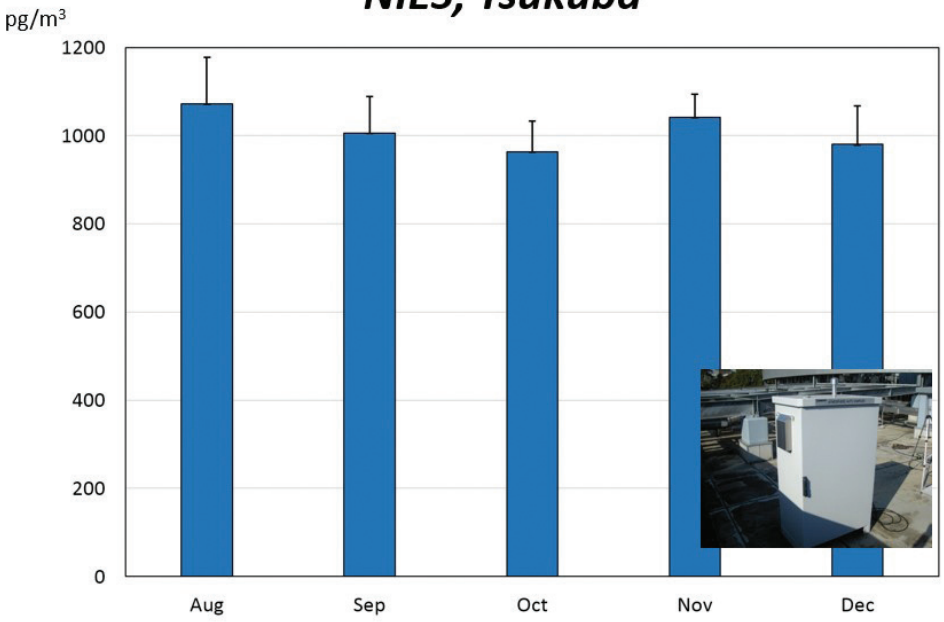
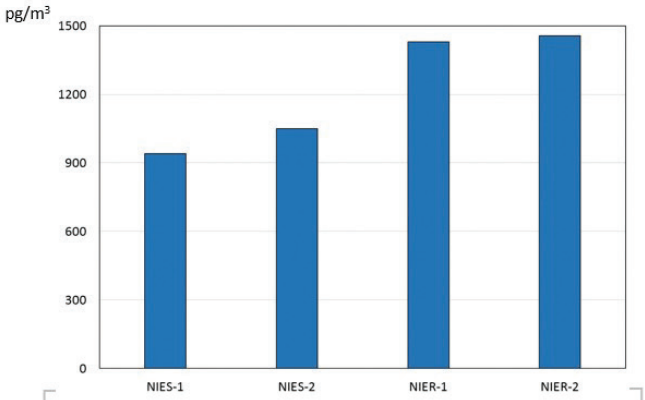
NIES, Tsukuba



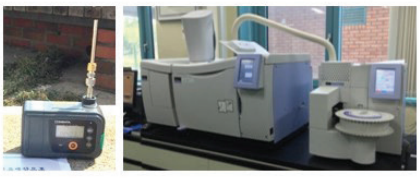
Samples were collected 5 days in a row
(vacuum volume 144L, *n* = 5 in each month)

Analysis of samples collected in NIER, Korea



September 14-15, 2017 (0.1L/min, 24h)

Gerstel TDU+GC/HRMS



PerkinElmer TD+GC/QMS

V–4 <2015-2017>

Cooperative research on analytical methods and environmental monitoring of emerging contaminants in water and sediments

Japan - **Katsumi IWABUCHI, Norimasa SENZAKI, Yuji KAWAMURA, Kiwao KADOKAMI, Norihisa TATARAZAKO**
Korea - **Jaean LEE, Byoungcheun LEE, Hyeonseo CHO**

1. Background

In addition to POPs/new POPs and other persistent chemicals with lipophilic properties, various emerging chemicals of concern include those with high water solubility, with low bioaccumulation or with easily degradable/biodegradable properties. For the proper monitoring and source identification of the latter group of contaminants, environmental monitoring of waters and sediments is needed.

Perfluorinated Chemicals like 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 sewage plants but in the river water by our studies.

We have already developed the technique to measure PFOS from one medaka. Therefore, Japan and Korea must cooperate to investigate quantity of PFOS/PFOA in several medium (soil, water, sediment, biota) in detail. We have succeeded to harmonize/communalize the measuring method, and to prepare the conditions with comparing the data between two countries.

We collected samples of medaka, surface water and the soil in Japan and Korea to measure PFOS and its related chemicals in them.

As a result, it was recognized that PFOS and its related chemicals accumulated to all material in environment, and it became clear that there was an area difference in Japan. And this year, as for the concentration of PFOS, a correlation was found between the whole body of the medaka and the water. Possibility was shown about monitoring of the POPs pollution in the environment using the medaka.

2. Research Plan

Japanese and Korean side will continue monitoring of perfluorochemicals for assessing the efficiency of recent regulatory action, and also for assessing potential effects of past usage. A compilation of information on simultaneous analytical methods of various contaminants will be conducted.

The research cooperation between Japan and Korea will include the followings

1) Surface water, sediment and Medaka will be collected in Japan and Korea, and clarify the possibility to biota monitoring PFOS/PFOA in the environment.

2) Start investigation on the multi-generation exposure study of PFOA with Medaka.

3) Brush up monitoring and toxicology test techniques and harmonize it between Japan and Korea.

3. Major Outcomes

In Japan and Korea, the field study of PFASs in various environmental samples comprising medaka fish, water and sediment in medaka habitat was performed from 2015 through 2017, and the monitoring results on PFASs bioaccumulation in Japanese and Korean aquatic environment were obtained.

<JAPAN>

1) In Japan, 15 types of PFASs were analyzed using LC-MS/MS. In this study, we found that concentrations of PFOS, PFNA, PFDA, and PFUdA in environmental water were correlated with them in medaka. PFASs were monitored at 5 fixed sites over the last 5 years (2013-2017), and the concentration trends of environmental water, sediment, and medaka were confirmed. As a result, there were few increasing or decreasing trends for the PFAS concentration, and they were almost flat. Accumulation of PFASs in sediments was correlated with organic matter (ignition loss). The bioconcentration factor (BCF) of PFASs in medaka was correlated with Log Kow.

2) Also in Japan, a comprehensive target screening method for 1000 substances in water was developed using newly developed mass spectral database for GC-MS (AIQS (Automated Identification and Quantification System) -GC) from 2015 through 2016. And in 2017, a target screening method for 500 polar substances in water was developed using LC-QTOF-MS (AIQS-LC). The developed methods provide a whole pollution picture of the surveyed area which is useful to identify substances that should be concerned and to clarify pollution sources and their contribution ratio to pollution.

<KOREA>

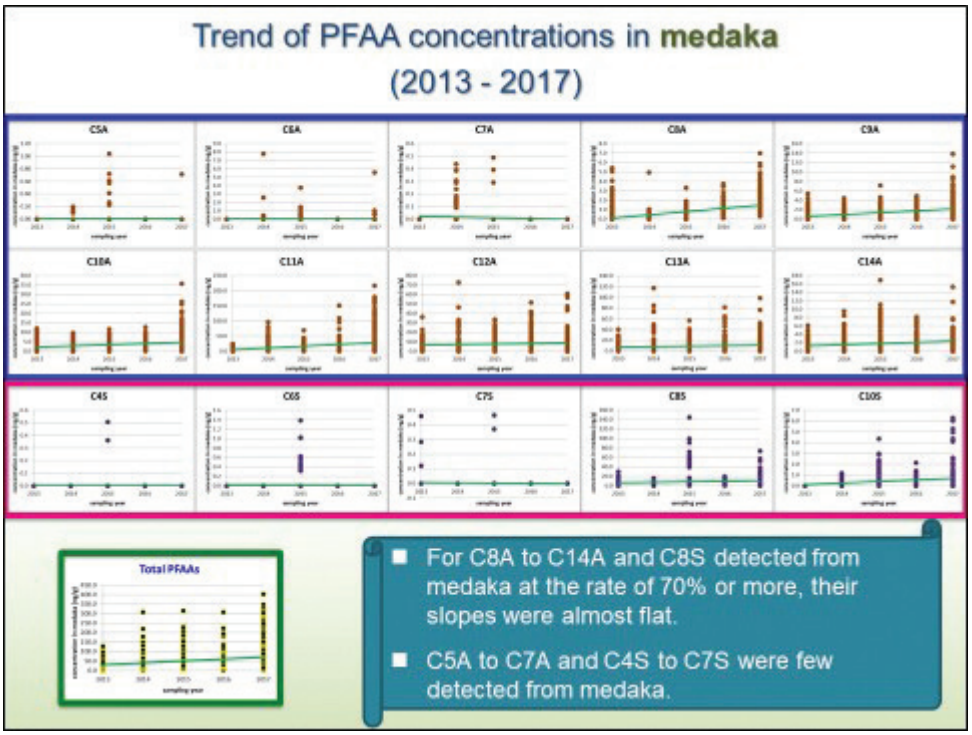
1) The concentration of PFASs in river water and river sediments were highest in Nakdong River and sulfonates (PFSA) was higher than carboxylates (PFCA) in all rivers. Compared with previous studies, the concentration of PFASs in river water and river sediment were the highest in 2015, and decreased in 2016 and increased in 2017.

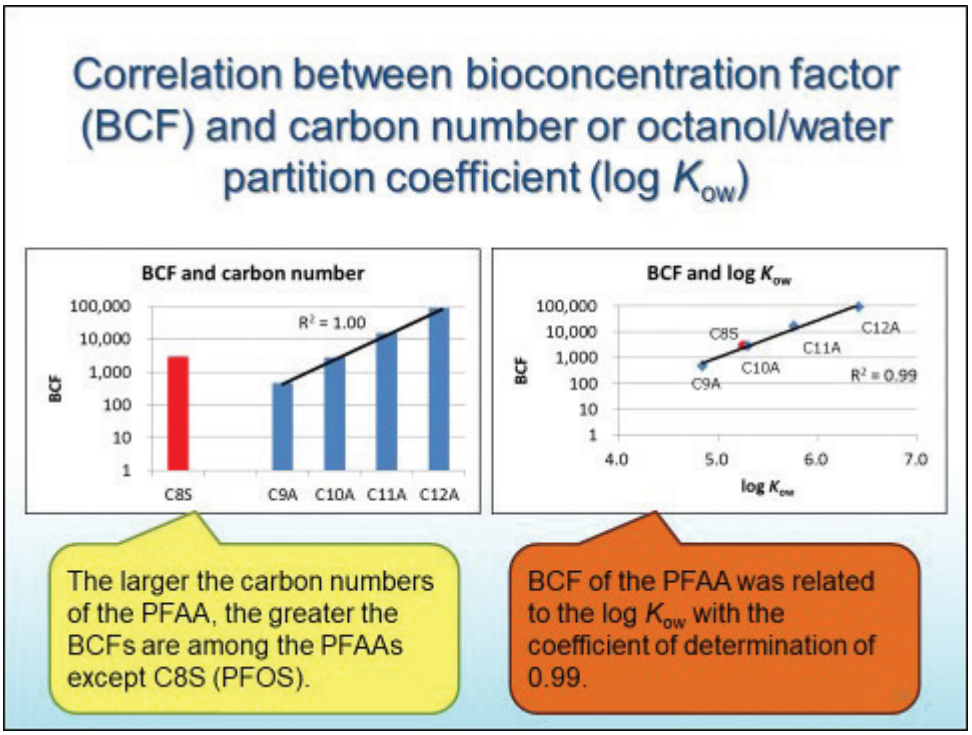
2) In 2017, PFOA and PFOS were detected at all sites in the medaka habitat water and not at all sites in the sediment. Compared with previous studies, the concentration of PFASs in medaka habitat water and sediment were the highest in 2015, and decreased in 2016 and increased in 2017.

3) PFOS were detected at all sites in the medaka whole body, and the mean concentration of PFASs in medaka whole body were the highest in 2014, higher in 2017 than in 2016, which was the lowest.

4) In the study from 2015 to 2017, the tendency of concentration of PFASs in the medaka whole body was higher in the sulfonates (PFSA) than in the carboxylates (PFCA).

Highlight Slides, JAPAN



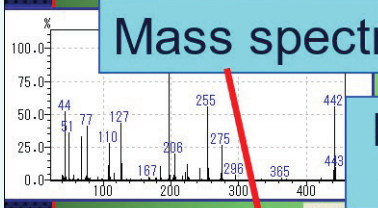


What is AIQS?

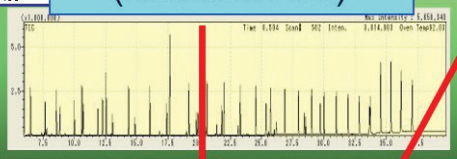
Data Registered in AIQS

Automated Identification and Quantification System with a DataBase

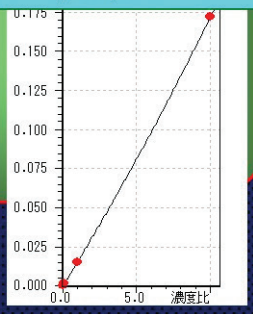
Mass spectra



Retention times (Relative RTs)



Calibration curves (IS)



Results

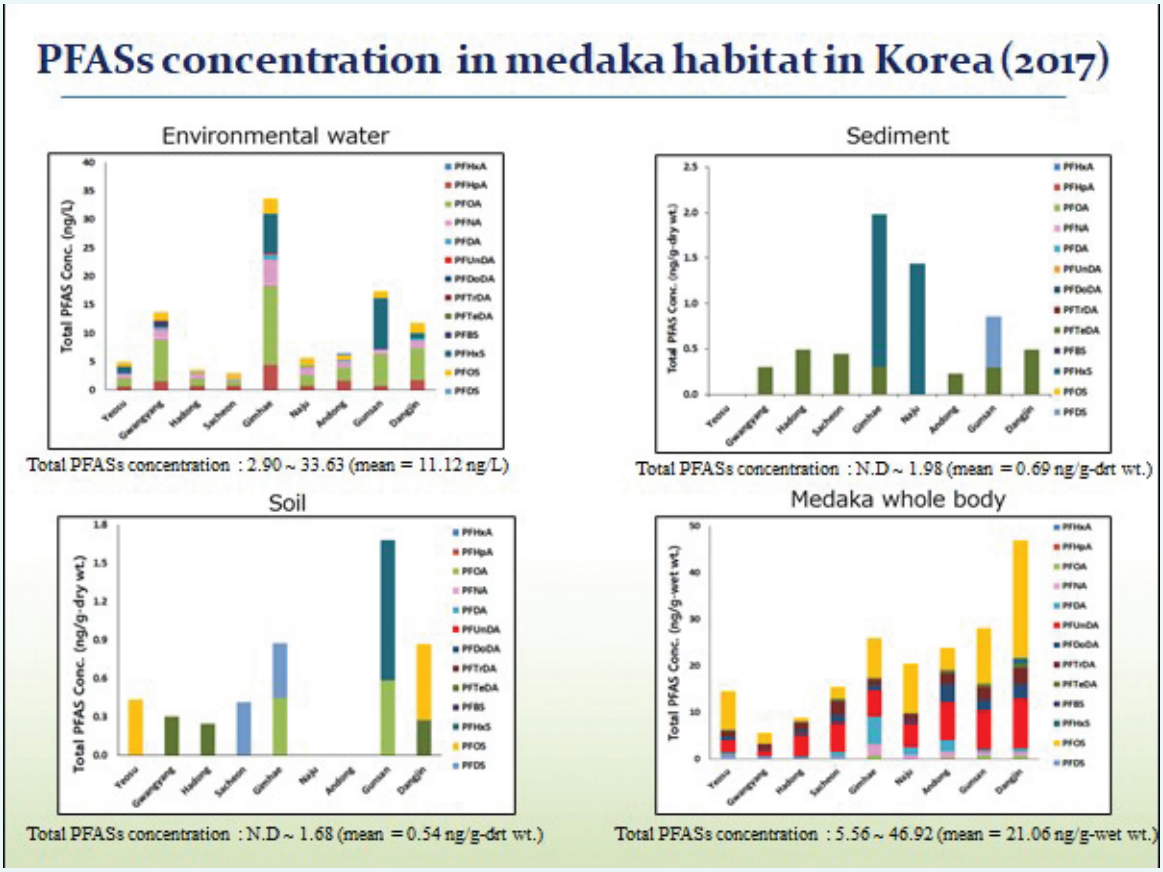
Substances in AIQS-GC

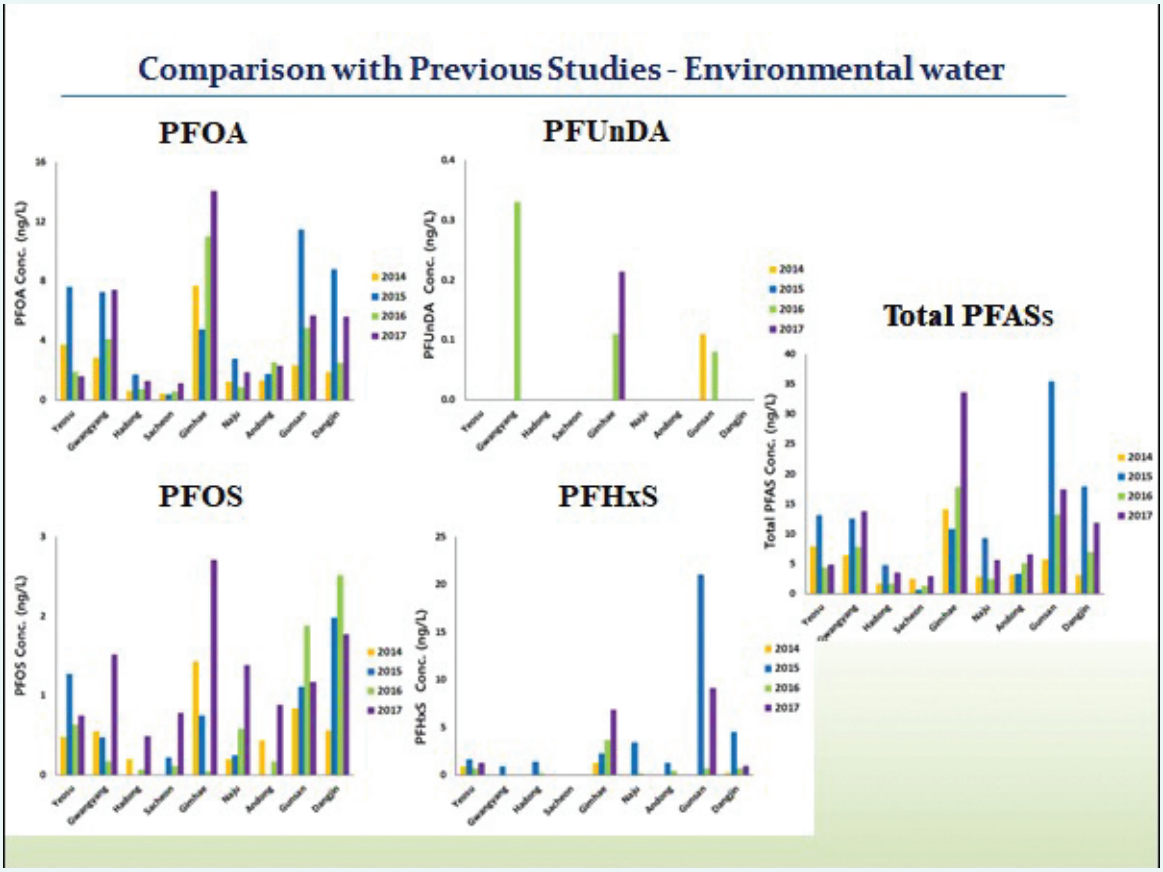
Class	Number
Chemicals consisting of C and H	195
Chemicals consisting of C, H and O	150
Chemicals containing N	113
Chemicals containing S	12
Chemicals containing P	8
PPCPs	14
Pesticides	451
Total	943

Substances in AIQS-LC

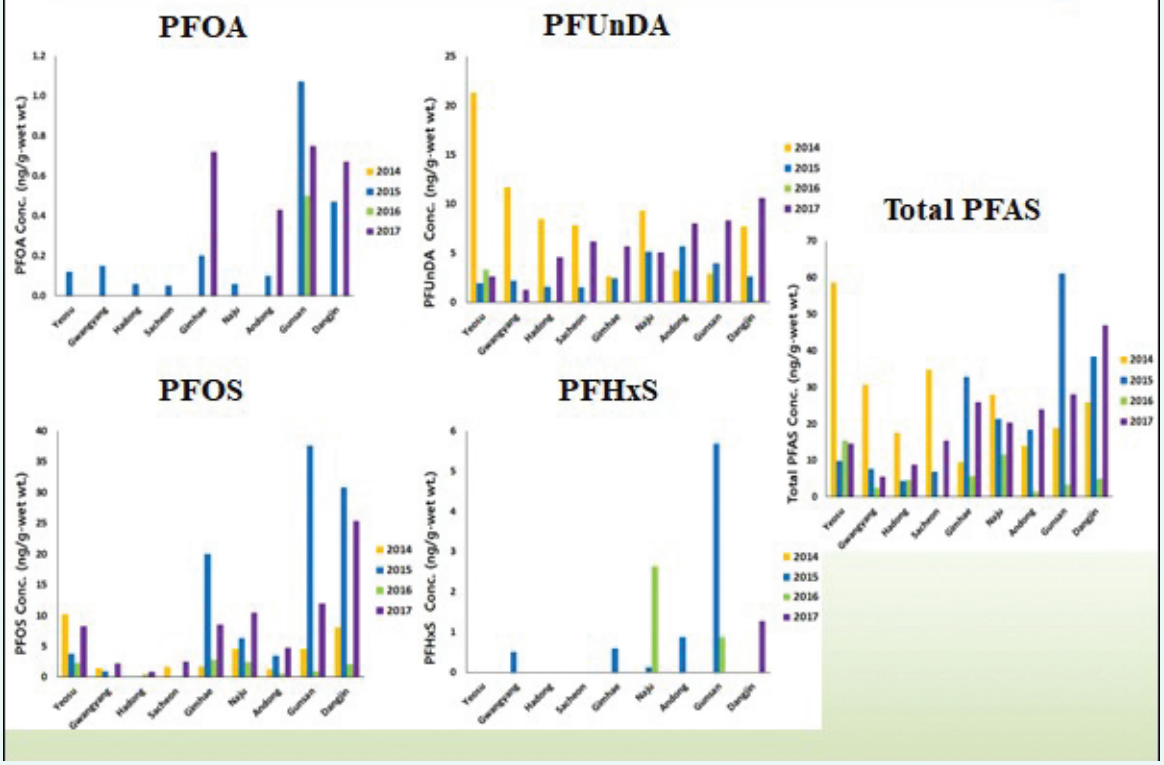
Class	Number
Pesticides	299
PPCPs (Pharmaceutical and Personal Care Products)	171
Industrial chemical	8
Others	13
Total	491

Using the two AIQS, thousands of substances in environmental samples can be analyzed quickly, cost-effectively, and resource-effectively without the use of reference standards.

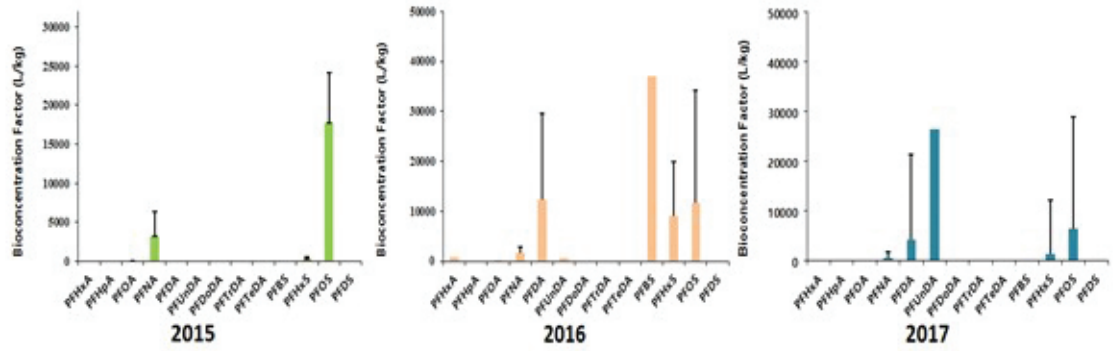

PFASs concentration in medaka habitat in Korea (2017)
Environmental water
Total PFAS Conc. (ng/L)
Total PFASs concentration : 2.90 ~ 33.63 (mean = 11.12 ng/L)
Sediment
Total PFAS Conc. (ng/g-dry wt.)
Total PFASs concentration : N.D ~ 1.98 (mean = 0.69 ng/g-drt wt.)
Soil
Total PFAS Conc. (ng/g-dry wt.)
Total PFASs concentration : N.D ~ 1.68 (mean = 0.54 ng/g-drt wt.)
Medaka whole body
Total PFAS Conc. (ng/g-wet wt.)
Total PFASs concentration : 5.56 ~ 46.92 (mean = 21.06 ng/g-wet wt.)
PFHxA
PFHpA
PFOA
PFNA
PFDA
PFUnDA
PFDoDA
PFTrDA
PFTeDA
PFBS
PFHxS
PFOS
PFDS
Yeosu
Gwangyang
Hadong
Sacheon
Gimhae
Naju
Andong
Gunsan
Dangjin


Comparison with Previous Studies - Environmental water
PFOA
PFOA Conc. (ng/L)
PFUnDA
PFUnDA Conc. (ng/L)
Total PFASs
Total PFAS Conc. (ng/L)
PFOS
PFOS Conc. (ng/L)
PFHxS
PFHxS Conc. (ng/L)
2014
2015
2016
2017
Yeosu
Gwangyang
Hadong
Sacheon
Gimhae
Naju
Andong
Gunsan
Dangjin

Comparison with Previous Studies – Medaka whole body



Trend of PFASs Bioaccumulation factor (BCF)



- ✓ Mean bioconcentration factor in 2017 (L/kg): PFUnDA (26,542) > PFOS (6,457) > PFDA (4,236) > PFHxS (1,320) > PFNA (683) > PFOA (123)
- ✓ BCF of PFOS (17,738) in the 2015 study, PFBS (36,928) in the 2016 study and PFUnDA (26,542) in the 2017 study was the highest.
- ✓ In the study from 2015 to 2017, the tendency of concentration of PFASs in the medaka whole body was higher in the sulfonates (PFSA) than in the carboxylates (PFCA).

VI–1 <2018~2020>

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

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

1. Background

As the Minamata Mercury Convention entered into force as international law (August 16, 2017), research cases tracking the source and movement path of mercury (Hg) using Hg concentration and stable isotope ratio are actively increasing worldwide. Hg is mainly emitted into the atmosphere by anthropogenic sources such as mining sites, thermal power plants using fossil fuels, and metal smelting plants. Hg in the atmosphere can be divided into three types: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate bound mercury (PBM). GEM and GOM are Together, they are called total gaseous mercury (TGM). GEM accounts for most (>75%) of atmospheric Hg, and its residence time in the atmosphere is relatively long, ranging from several months to a year, so it plays an important role in the long-distance movement of Hg. On the other hand, GOM and PBM are removed from the atmosphere by precipitation, so they have a relatively short residence time of several days to weeks.

Hg has seven stable isotopes, and mass variation is influenced by MDF (δ, mass-dependent fractionation) and MIF (Δ, mass-independent fractionation). MDF is mainly affected by oxidation-reduction, adsorption-desorption reactions, volatilization, etc., and affects the δ^{202}Hg isotope ratio. MIF is mainly generated by photochemical reactions and affects the Δ^{199}Hg and Δ^{201}Hg isotope ratios. Therefore, since the stable isotope ratio of Hg in the atmosphere is influenced by physical and chemical reactions during anthropogenic emission sources and behavior, it is possible to trace the pollution source and movement path of Hg through sufficient research. In previous studies, the adsorption trap-thermal desorption method and the impinger method were used to analyze the isotope ratio of Hg in the atmosphere. The impinger collection method uses the Ontario-Hydro method to collect mercury by species (Hg(II), Hg(0)). The adsorption trap method collects mercury using a gold trap or carbon trap. However, because the concentration of gaseous mercury in the atmosphere is very low (~ several ng/m3), long-term collection is required to collect the amount of Hg required for stable isotope ratio analysis, and loss of Hg must be prevented during the pretreatment process for Hg re-collection.

2. Research Plan

1) Both NIER in the republic of Korea and NIES in Japan will cooperate to develop the analytical technique for higher sensitivity of Hg isotope ratios even at lower Hg concentration in atmospheric and plant samples in order to reveal the environmental cycling of Hg in the East Asia region.

2) Additionally, both institutes conducted to develop effective sampling and pretreatment methods for Hg isotope analysis along with analyzing a wide variety of environmental samples associated with atmospheric Hg in a regional and global Hg cycling.

3) NIER tested an active carbon-based Hg traps and gold-coated quartz sand Hg traps.

4) For the accuracy of the Hg isotope values, harmonization of QAQC procedure will be jointly conducted.

3. Major Outcomes

<KOREA>

1) In order to improve the efficiency of the previously performed trap method, we compared carbon trap and gold trap. As a result of testing using standard materials (NIST3133, 0‰), the carbon trap showed a mercury recovery rate of 97.1% and the mercury isotope ratio ranged from -0.07 to 0.05‰, while the gold trap showed a mercury recovery rate of 96.8% and a Hg isotope ratio ranged from 0.0 to 0.06‰, indicating a higher mercury recovery rate and less isotope ratio fractionation.

2) In order to analyze the Hg isotope ratio of total gaseous Hg (TGM), and efficient sample collection method (air gas flow, trap time, active carbon-based and gold-coated quartz sand traps) was evaluated.

3) In the result, it is suitable to collect TGM sample with less isotope fractionation using a gold trap at 2 L/min flow rate for one week. Because gold traps had 0.5 to 10 times higher Hg concentration in comparison with carbon trap, and showed significantly difference in Hg isotope ratio between traps.

4) Additionally, NIER found that TGM samples reflected values similar to Hg transported from long distance and influenced by anthropogenically emitted Hg.

<JAPAN>

1) The Hg isotope analytical system at NIES was optimized to improve intensity and precision by means of adjustments of carrier argon gas flow rates of the introductory system and electrostatic lens of an analytical instrument.

2) The sensitivity of the NIES system was improved by approximately 1.7 times, and the analytical errors were lowered by approximately half.

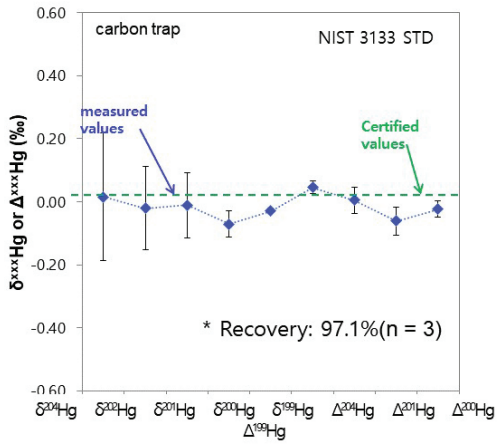
3) Hg isotope ratios of plant litters and tuna fish muscle tissues were determined to evaluate different sources of bioaccumulating Hg.

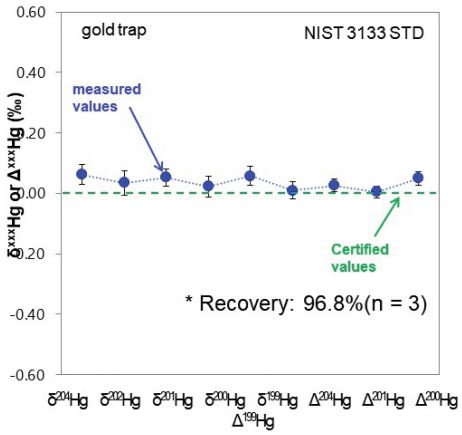
4) The determined litter Hg isotope ratios indicated that Hg in litter was mainly from atmospheric Hg, and their odd MIF values were slightly negative in Δ^{200}Hg and positive in Δ^{204}Hg. On the other hand, the determined fish odd MIF values were slightly positive in Δ^{200}Hg and negative in Δ^{204}Hg, suggesting different pathways and chemical transformation of bioaccumulating atmospheric Hg.

5) These findings indicated that Hg isotope ratios of environmental samples were useful indicators for distinguishing Hg sources and understanding Hg accumulating pathways.

Lab experiment (gaseous Hg sampling system)

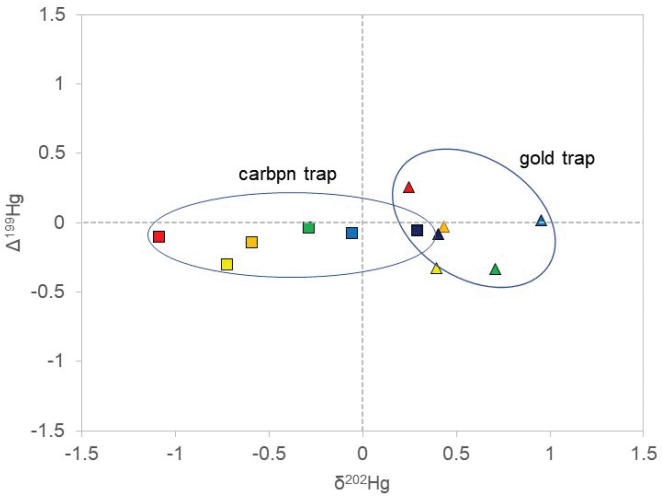
Hg isotope value between carbon and gold trap





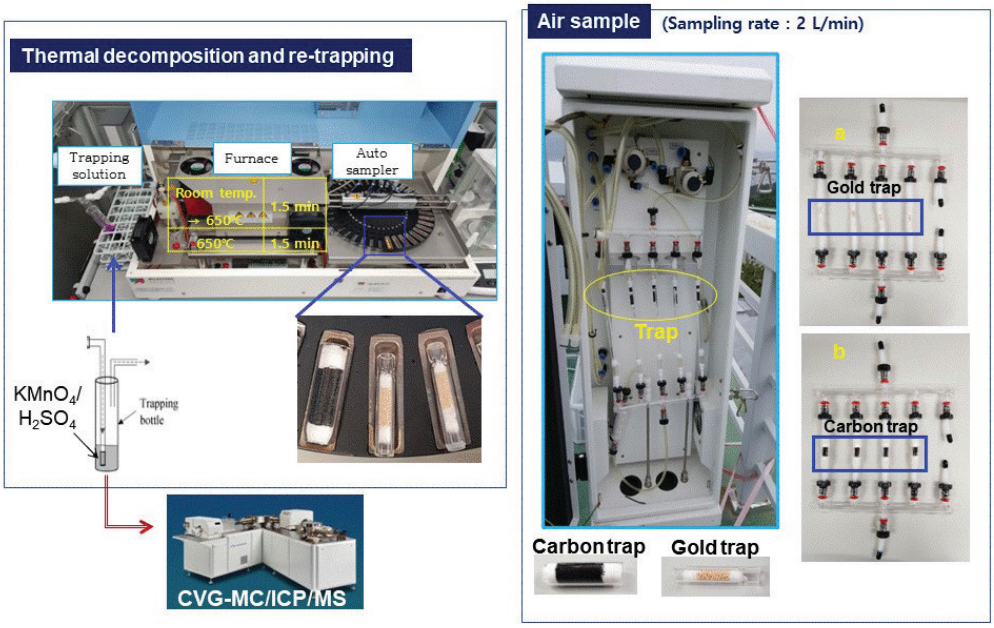
Field test (gaseous Hg sampling system)

Hg stable isotopes (Carbon trap vs Gold trap)



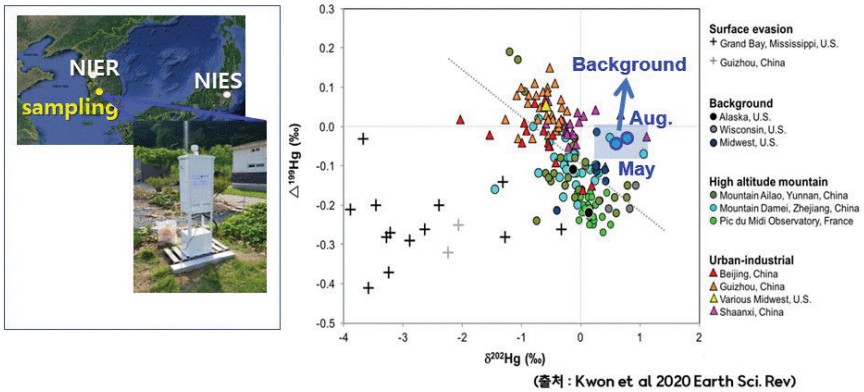
Gaseous Hg sampling system)

➢ Total gaseous Hg collection (Carbon trap vs Gold trap)



Field test (gaseous Hg sampling system)

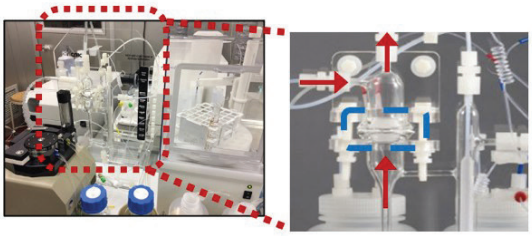
Atmospheric Hg is affected by long distance transport of Hg



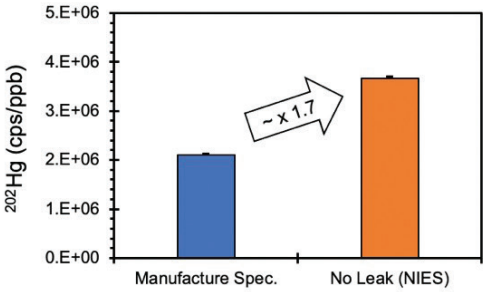
(출처 : Kwon et al 2020 Earth Sci. Rev)

Optimizations of Hg Isotope Analytical Systems (NIER and NIES)

A) Sample Introduction System
(HGX-200)



Higher Sensitivity !

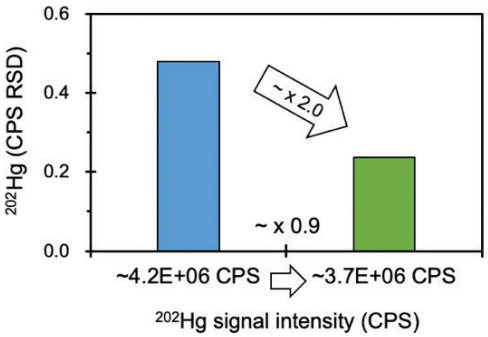


B) Instrument Settings

- Ar Gas Flow Rate (L/min)
- Electrostatic Lens (eV)

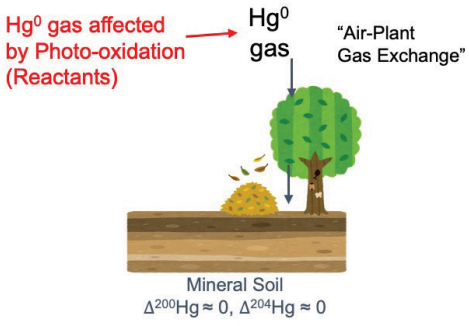
➢ These parameters are directly related to signal intensities.

Higher Precision !



Hypothesis

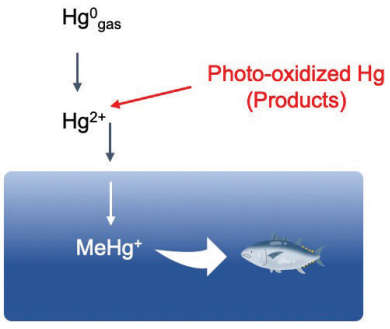
Terrestrial Ecosystems



Litter Soil; $\Delta^{200}Hg \approx$ or < 0 & $\Delta^{204}Hg \approx$ or > 0 ?

Measured at NIER

Marine Ecosystems

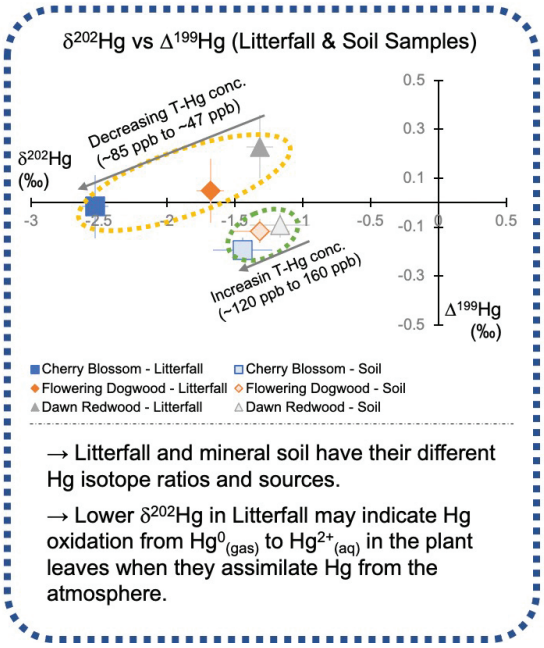


Fish; $\Delta^{200}Hg > 0$ & $\Delta^{204}Hg < 0$?

Measured at NIES

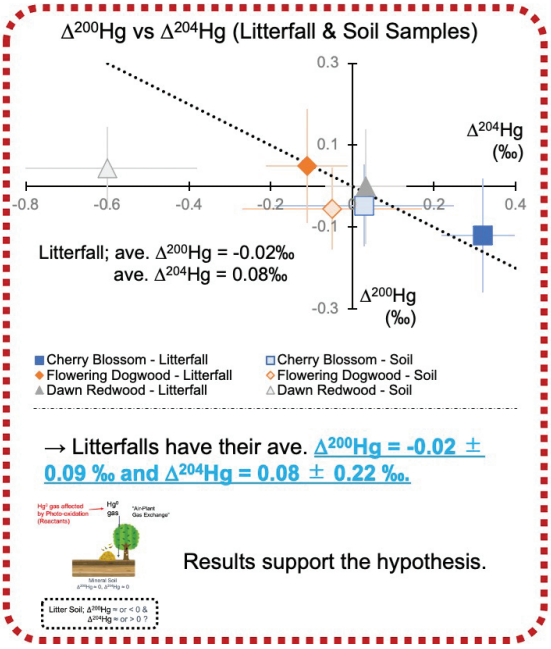
Δ^{200}Hg vs Δ^{204}Hg in Litter & Mineral Soils

Sample prepared at NIES & Measured at NIER in 2020



→ Litterfall and mineral soil have their different Hg isotope ratios and sources.

→ Lower δ^{202}Hg in Litterfall may indicate Hg oxidation from $Hg^0_{(gas)}$ to $Hg^{2+}_{(aq)}$ in the plant leaves when they assimilate Hg from the atmosphere.



→ Litterfalls have their ave. Δ^{200}Hg = -0.02 ± 0.09 ‰ and Δ^{204}Hg = 0.08 ± 0.22 ‰.

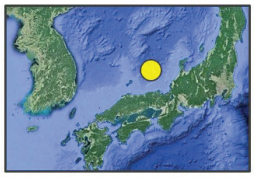
Results support the hypothesis.

Δ^{200}Hg vs Δ^{204}Hg in Pacific Bluefin Tuna

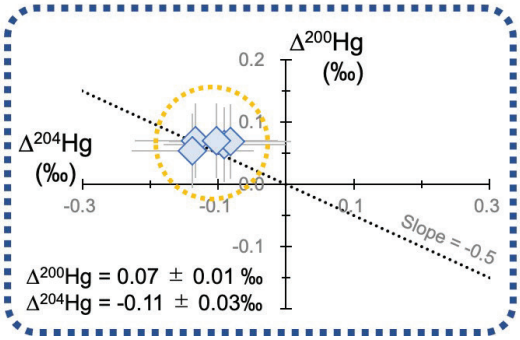
(Hg Isotope Signatures of Atmospheric Hg Source?)

- "Δ^{200}Hg > 0" & "Δ^{204}Hg < 0" indicate that the Hg undergoes Photo-oxidation reactions with halogen (Br & Cl, maybe more) (Sun et al., 2016).
- Photo-oxidation (Hg^0 + UV-Light → Hg^{2+} + $2e^-$) takes place in the atmosphere.

Tuna muscle samples from a near-shore area of Japan;



MeHg Conc.;
0.56 ± 0.03 mg/kg (wet) n = 5



- Bioaccumulated MeHg in the Tuna samples underwent 1) Photo-oxidation & 2) Methylation.
- Atmospheric Hg may affect the top predator fish Hg.

This information may be useful for policy makers and general public.

VI–2 <2018~2020>

Cooperative research on bioaccumulation of emerging contaminants in fishes

Korea – Hyeonseo CHO, Kyunghwa PARK, Kyungtae KIM, Byoungcheun LEE, Byeongwoo LEE, Hyunggeun PARK
Japan – Takeo SAKURAI, Noriyuki SUZUKI, Norihisa TATARAZAKO

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 and other related chemicals in both countries. Based on this common understanding, cooperative researches on long-range-transport modeling and bioaccumulation of these compounds had been conducted, including those with higher water solubility and various emission sources.

This cooperative research will study the occurrence, behavior, and bioaccumulation of new POPs and other emerging contaminants in the aquatic system, by experimental, field-study, and modeling approaches, and thus contribute to the understanding and modeling of the multi-medium behavior of these compounds.

2. Research Plan

1) Some of the perfluoroalkyl acids (PFAAs) are currently under consideration to be listed as persistent organic pollutants (POPs) under the Stockholm Convention, in addition to perfluorooctanesulfonate (PFOS) which was listed in 2009 and perfluorooctanoate (PFOA) which was listed in 2019. A limited number of studies on these candidate POPs and related compounds has been performed to investigate their occurrence, distribution, and bioaccumulation in the environment compared to conventional POPs. It is essential to understand the occurrence and fates of these emerging POPs in the environment.

2) Bioaccumulation of emerging chemicals including PFAAs in Korean freshwater systems will be studied. The Japan side will study bioaccumulation of PFAAs by means of modeling methods. The Korean side will continue the study about accumulation and monitoring of emerging contaminants in Korean aquatic environment including fish. Finally, both sides will evaluate the applicability of the developed model in freshwater ecosystem.

3. Major Outcomes

We worked on the bioaccumulation of perfluoroalkyl acids (PFAAs) in Korean freshwater systems. The Korean side performed the field bioaccumulation monitoring of PFAAs and food-web structure in aquatic ecosystem in two main rivers including the Namhan river. Some results of bioaccumulation factor (BAF and BMF) through a river food web were evaluated. PFOS was over the very bioaccumulative level, and high BMF values in the species at the

trophic levels 3 and 4 showed that higher trophic levels tend to show higher BMF values. The Japan side worked on modelling the bioaccumulation of PFAAs. The kinetic and physiological parameters were estimated. Food-web structure was incorporated by the cooperation of the Korean side. The general properties of the model were examined by a preliminary model run. Together, the model predictions were compared with the measured concentrations. The fit of the model predictions was good for middle-chain compounds but poorer for shorter- and longer-chain compounds where kinetic data are limited. The applicability of the model was further evaluated by applying to other freshwater ecosystems.

Some specific results are listed below.

<KOREA>

Bioaccumulation (BAF)

1) In Yeoju, the highest BAF (L/kg) was found in the leopard mandarin fish (21,375), while the lowest BAF value (381) was found in the catfish.

2) BAF values were over the very bioaccumulative level with a high accumulated PFOS.

3) In each trophic level, BAF has an increased trending between species, especially PFOS values.

Biomagnification (BMF)

1) In Yeoju, in case of predator's prey is zooplankton.

2) The high BMF values of PFASs was found in pond loach, Gobiobotia macrocephala, and crab with the high values of long-chain PFASs as PFUnDA, PFDoDA, PFTrDA and PFOS.

3) High BMF values of the species in the trophic level 3 and 4 showed that higher TL tend to higher BMF values.

4) The low BMF values of PFOA was found in almost species while other compound is not available.

5) The PFAA uptake pathway study of these organisms and further monitoring are necessary to understand the very high BMF of long-chain PFAAs in several species.

<JAPAN>

1) We worked on modeling bioaccumulation of PFAAs in aquatic food webs.

2) Kinetic parameters were estimated based on the analysis of reported experimental values in literature.

3) Food-web structure was incorporated based on general information on the sampled species.

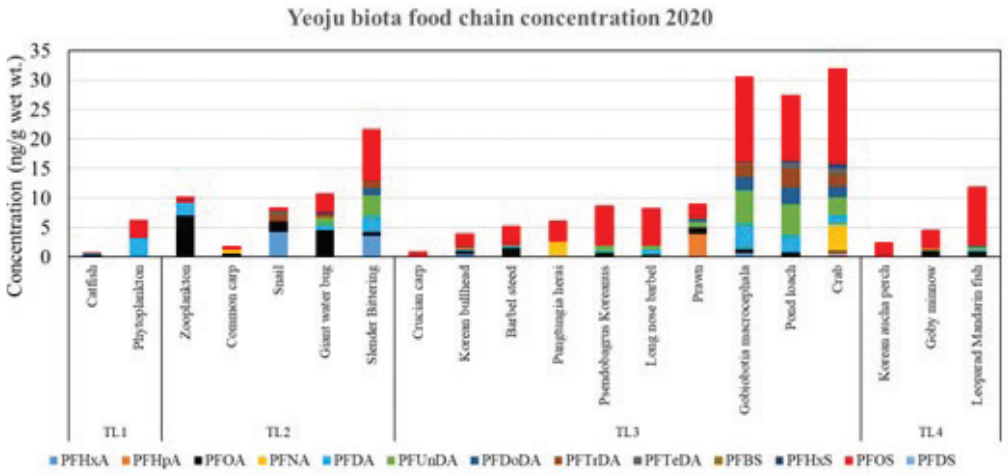
4) Fit of model predictions varied among compounds. Poorer fit to measured values for shorter- and longer chain compounds, for which experimental data are limited.

5) Similar levels of applicability of the model to other aquatic systems were demonstrated.

6) Further study is needed for kinetics. For shorter- and longer-chain, as well as alternative compounds. For animals other than fish; difference in values and trends with alkyl-chain length suggested (incl. daphnia and sandworm).

Highlight Slides, KOREA

PFAAs concentrations in the food chain samples in Yeoju, Korea



- The highest PFASs concentration (ng/g wet ww) was 32.01 in Crab while the lowest level PFASs was found in Catfish (3.79).
- PFOS was found in all species with a range of 0.25~16.22 (Catfish~Crab)
- PFOA was found in 16/20 species (except Phytoplankton, Crucian crap, Pungtungia herai and Korean aucha perch).

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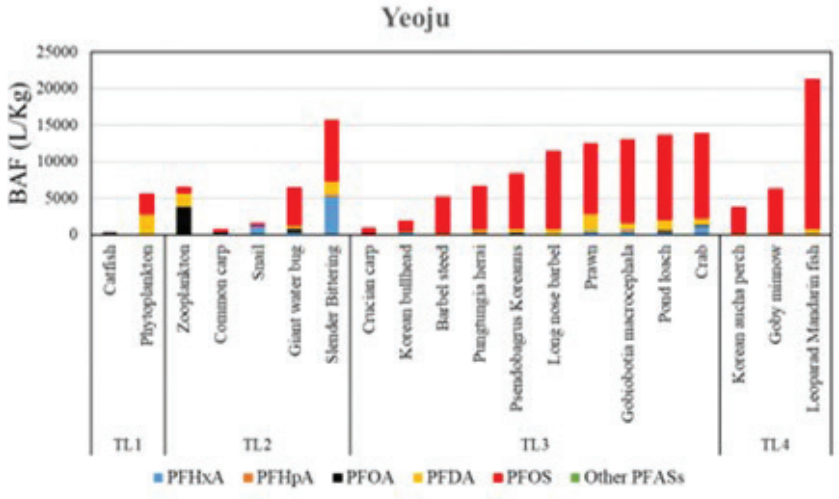
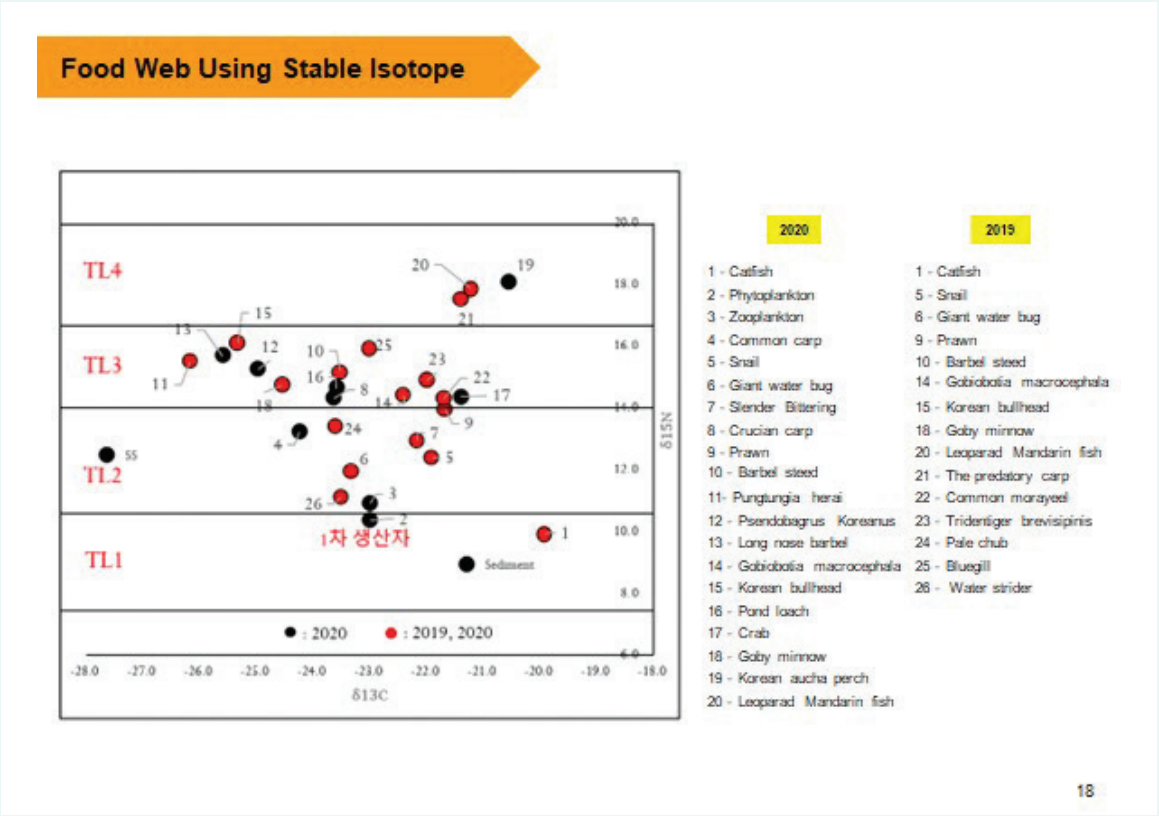
Bioaccumulation factor(BAF) in the food chain samples in Yeoju, Korea



15

Tropic levels in the food chain samples in Yeoju, Korea



Biomagnification Factor (BMF) of PFAAs in the food chain samples in Yeoju, Korea

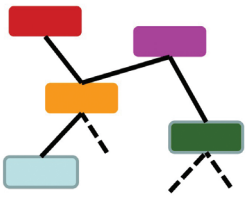
Case 4 - Zooplankton is the predator's prey (2020)

	BMF	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS
TL-1	Catfish	NA	NA	0.32	NA	NA	NA	NA	NA	NA	NA	NA	0.11	NA
TL-2	Common carp	NA	NA	0.45	NA	NA	NA	NA	NA	NA	NA	NA	0.28	NA
	Slender Bittering	NA	NA	0.70	NA	NA	3.86	2.34	2.20	NA	NA	NA	4.00	NA
TL-3	Crucian carp	NA	NA	NA	NA	NA	0.19	NA	NA	NA	NA	NA	0.30	NA
	Barbel steed	NA	NA	1.45	NA	NA	0.22	0.29	NA	NA	NA	NA	1.43	NA
	Pungtungia herai	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.58	NA
	Pseudobagrus Koreanus	NA	NA	0.68	NA	NA	1.11	NA	NA	NA	NA	NA	3.03	NA
	Long nose barbel	NA	NA	0.32	NA	NA	0.74	NA	NA	NA	NA	NA	2.84	NA
	Gobiobotia macrocephala	NA	NA	0.58	NA	NA	6.05	4.48	4.67	NA	NA	NA	6.53	NA
	Korean bullhead	NA	NA	0.44	NA	NA	0.37	NA	NA	NA	NA	NA	1.10	NA
	Pond loach	NA	NA	0.76	NA	NA	5.65	5.65	7.47	NA	NA	NA	4.98	NA
	Crab	NA	0.11	0.23	NA	NA	3.28	3.47	5.11	NA	NA	NA	7.25	NA
TL-4	Goby minnow	NA	NA	1.06	NA	NA	NA	NA	NA	NA	NA	NA	1.45	NA
	Korean aucha perch	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.11	NA
	Leoparad Mandarin fish	NA	NA	0.81	NA	NA	0.57	0.61	NA	NA	NA	NA	4.48	NA

*NA: Not available

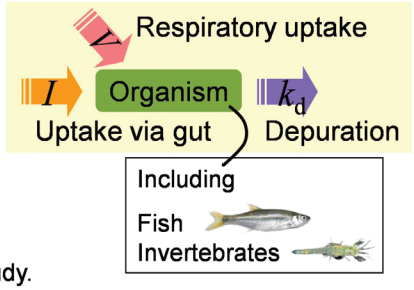
Model framework

- Food-web model
  - Predator–prey network of species
  - Species are represented by an organism-level model.



- Organism-level model
  - Mass-balance, 1st-order kinetics, whole body as one compartment[1,2].
    - Respiration and ingestion: two major pathways of uptake.
    - Depuration: another key process controlling bioaccumulation.

$$\frac{dC_b}{dt} = \frac{V}{W}\alpha_{ur}C_w + \frac{I}{W}\alpha_{ug}\sum_i (p_i C_{fi}) - (k_d + k_g)C_b$$



- C_b: Whole-body concentration
- Parameters: 4 physiological (I, V, W, k_g);
  3 kinetic (α_{ur}, α_{ug}, k_d); 1 food web (p);
  2 environmental (C_w, C_f).
- We applied a steady-state calculation[2] in this study.

1) Norstrom RJ et al. 1976. 2) Arnot JA and Gobas FAPC. 2004.

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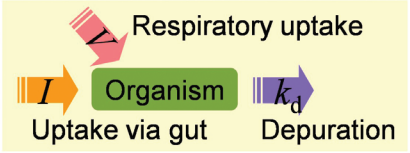
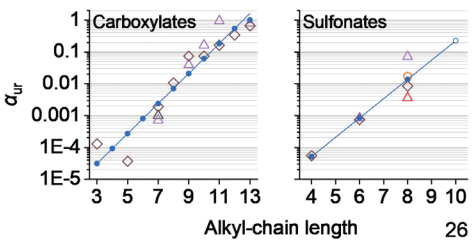
Slide presented at the 20th Joint Symposium on POPs Research (23 February 2021)

Kinetic parameters

$$\frac{dC_b}{dt} = \frac{V}{W}\alpha_{ur}C_w + \frac{I}{W}\alpha_{ug}\sum_i (p_i C_{fi}) - (k_d + k_g)C_b$$



- Kinetic parameters were estimated based on analysis of reported values from kinetic experiments.
  - α_{ur} (respiratory UE); α_{ug} (gut UE); k_d: (depuration RC)
  - Single representative value was determined.
  - Updated: Quality papers/reports selected based on technical criteria.
  - QSPR based on alkyl-chain length applied where appropriate.
  - Fish: 10 papers, 4 species
  - Plankton BCF+BAF combined (freshwater 4 papers).
  - Invertebrates
    - α_{ur}, α_{ug}: Fish data (limited invert. data)
    - k_d: Invertebrate (3 papers) + fish data



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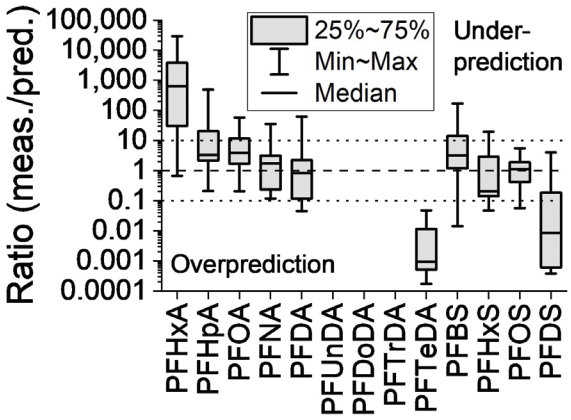
Slide presented at the 20th Joint Symposium on POPs Research (23 February 2021)

Predicted and measured PFAA concentrations



Fit	Criteria (ratio)
Good	Interquartile range 0.1–10
Slightly under- or over-predicted	median 0.1–10, but 25%ile <0.1 or 75%ile >10
Under- or over-predicted	median < 1 or > 10

Note: 25 species for each compound.
Half DL was assigned to values <DL.

- Median of ratio ranged 0.00092–640.
  - Median of most compounds 0.1–10 (excl. PFHxA, PFTeDA, PFDS)
  - Interquartile range 0.1–10: PFNA, PFDA, PFHxS, PFOS
- Kinetic data are limited for shorter- and longer-chain PFAAs.
  - ACL-based QSPR may not be working well.

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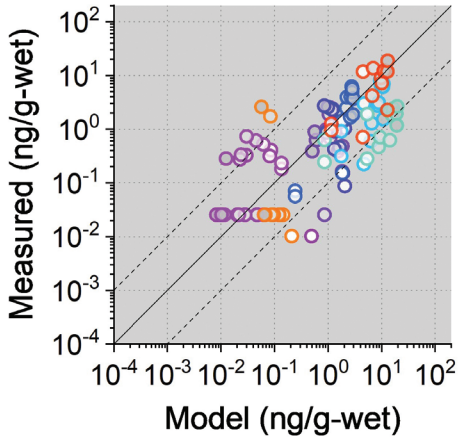
Slide presented at the 20th Joint Symposium on POPs Research (23 February 2021)

Applicability of the model evaluated (1)



PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, (PFTrDA), (PFTeDA), (PFBS), PFHxS, PFOS, (PFDS)

Note: Measured data are taken from Xu et al. 2014, Environmental Pollution 184, 254. (Taihu Lake, China)
- Water, sediment, and 13 species (1 bird excluded).
- Average of the reported values used.
- Values <DL plotted as half DL.

- Compared with PFAA conc reported for a freshwater ecosystem in China (Xu et al. 2014).
  - The same general food-web structure applied.
  - Overall good agreement between measured and modeled conc.
  - Underpredicted: PFHpA

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Slide presented at the 20th Joint Symposium on POPs Research (23 February 2021)

VI–3 <2018~2020)>

Cooperative research on environmental monitoring of POPs and other priority pollutants

Japan – Yoshikatsu TAKAZAWA, Yasuyuki SHIBATA
Korea – Younghee KIM, Donghoon KIM, Youngsun DO

1. Background

Article 16 of the Stockholm Convention requires the Parties to carry out environmental monitoring of priority media including air, and submit "comparable" monitoring data to the Secretariat for the effectiveness evaluation. In East Asian countries, air POPs monitoring program and POPs training workshop have been conducted to support the Convention. In addition to the 12 initial POPs, as 16 new POPs have been added to the Convention and several candidates are under review, the development and harmonization of POPs and new POPs monitoring methods are needed. Japan and 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

Japan and Korea will develop and share the analytical methods of PFASs, PBDEs and SCCPs was adopted. We will make efforts so that our cooperative results will be effective parts for the Stockholm Convention. Both countries also monitored atmospheric HCHs and HCB at the background sites of each country. Furthermore, the atmospheric levels of PFASs and PBDEs at the background sites of both countries will be also monitored and compared.

3. Major Outcomes

<KOREA>

1) Analytical methods of SCCPs were shared and developed for various environmental matrices. GC/ECNI-MS analysis method using electron capture negative ionization was mainly used, and quantification method using sensitivity coefficient method using correlation between total chlorine content (%) and total sensitivity coefficient or multiple regression method was used.

2) Korea monitored atmospheric PFASs in the Jeju Island during 2019 by using high-volume air sampler. Air samples were extracted with methanol, purified with wax cartridges, and analyzed by LC-MSMS for a total of 29 PFASs. In Jeju, Korea, PFBA and FOUEA were found to be mainly distributed in the gas phase, while PFOA, PFOS, and FOSA were found to be distributed in the particle phase.

3) The average concentration of OCPs in Jeju Island showed that hexachlorobenzene, pentachlorobenzene, and endosulfan were detected in high concentrations. Heptachlor,

chlorodanes, and drins are found at very low concentrations, with detection rates of less than 50%.

<JAPAN>

1) Airborne total HCHs at Hateruma ranged from 5.3 to 26 pg/m^3 in 2018. Total concentration of HCB and PeCBz also varied from 92 to 270 pg/m^3.

2) Air monitoring in Okayama prefecture indicated that release of HCBD continued with high concentration (geometric mean 2,800 pg/m^3).

3) Japan monitored PFASs by using high volume air sampler during September to December in 2019. 8:2 Fluorinated telomer alcohol (8:2FTOH) was the most dominant PFAS precursor, and the concentration varied from 59-150 pg/m^3. Other important precursors (FOSA and FOSE) of PFASs were also detected every month.

Highlight Slides, KOREA

Analytical flow chart of short-chain chlorinated paraffins (SCCPs) in the environment

Analytical methods of SCCPs

SCCPs (thousands of isomers are generated)

↓

Difficult to separate peaks using GC,
Homolog only analysis available (number of C, Cl)

↓

Tendency the higher the chlorine content,
the higher the device detection value
Under-or over-evaluated according to the chlorine content

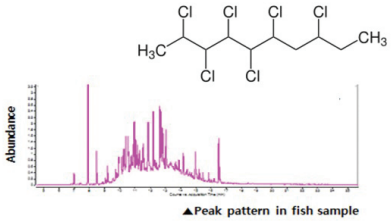
↓

Correct with calibration solutions

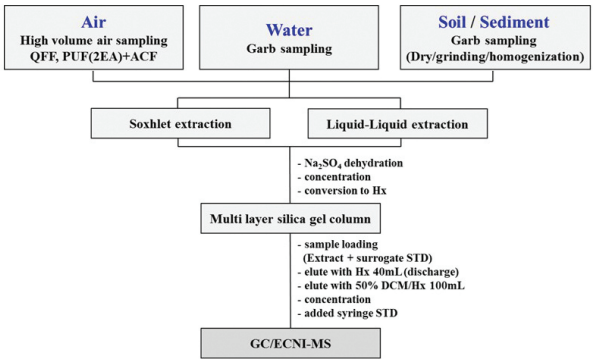
- **Total response factor quantification**
- **Multiple regression calibration (ISO)**

↓

GC/ENCI-MS



▲Peak pattern in fish sample



Analytical flow chart of per- and polyfluorinated substances (PFAS) in air sample

PFASs – *pretreatment procedure*

High-volume Air Sampling
(GFF, PUF(2ea), ACF)

700 L/min for 24h

Soxhlet extraction
with **MeOH** for 24 h

Concentrate to 1mL

SPE (WAX cartridge)

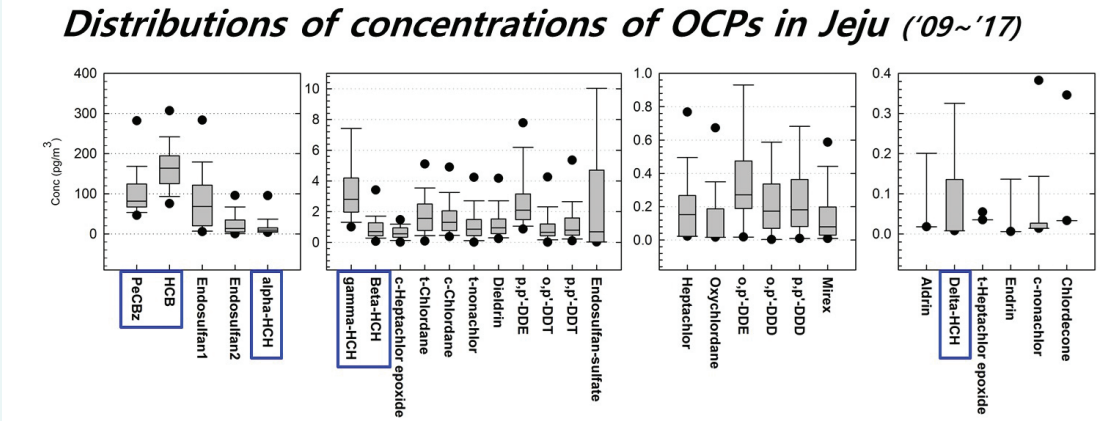
1. **conditioning** with
   (1) 4 mL 0.1% NH_4OH/MeOH
   (2) 4 mL MeOH
   (3) 4 mL H_2O
2. **load the extract** dissolved in 10% MeOH/DIW
3. **dry** for 30 sec
4. **wash** with
   (1) 4 mL 0.025 M Acetate buffer
   (2) 4 mL MeOH
5. **Elution** with 4 mL 0.1% NH_4OH/MeOH
6. **Concentrate to 1mL**
7. **Filtering**

LC-MS/MS
(ESI negative mode)

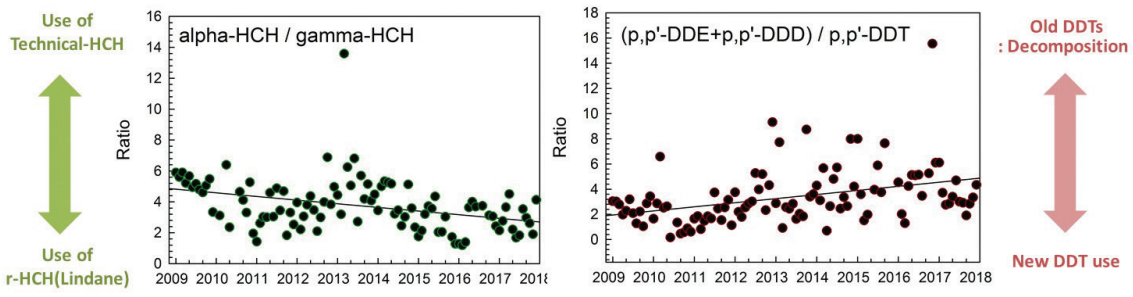
LC-MS/MS (29 PFASs)

PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS,
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA,
PFUnDA, PFTrDA, PFTeDA, PFHxDA, PFOcDA,
FOSA, N-EtFOSA, N-MeFOSA, FOSAA, N-EtFOSAA,
N-MeFOSAA, FOUEA, FOET

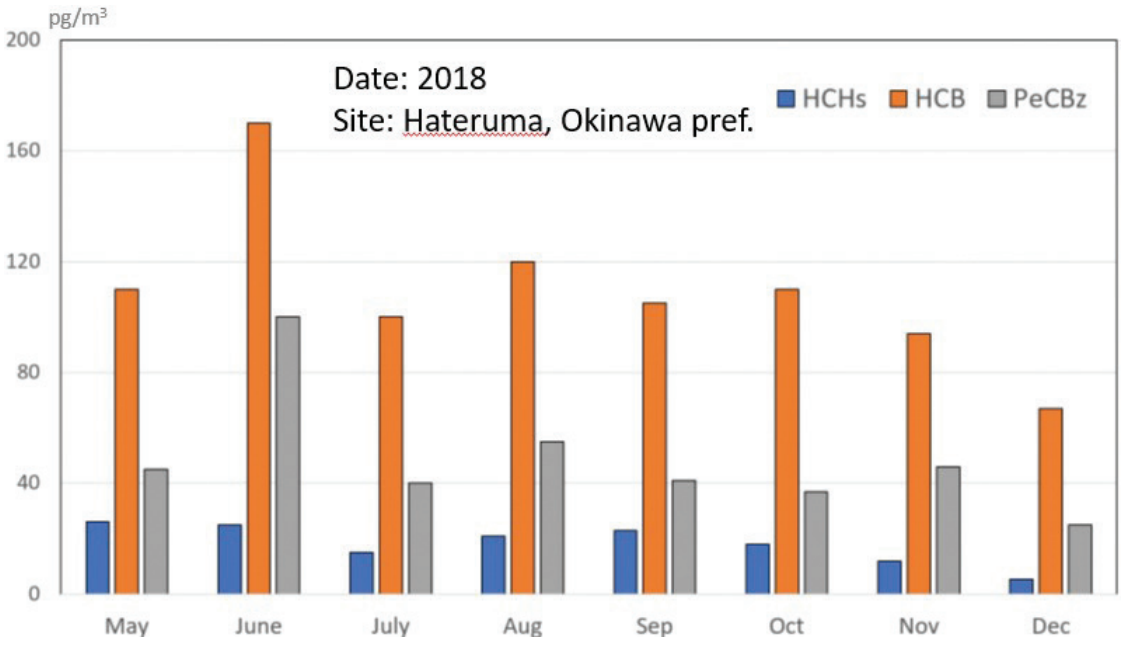
Distributions of atmospheric OCPs concentrations in Jeju (‘09~’17)

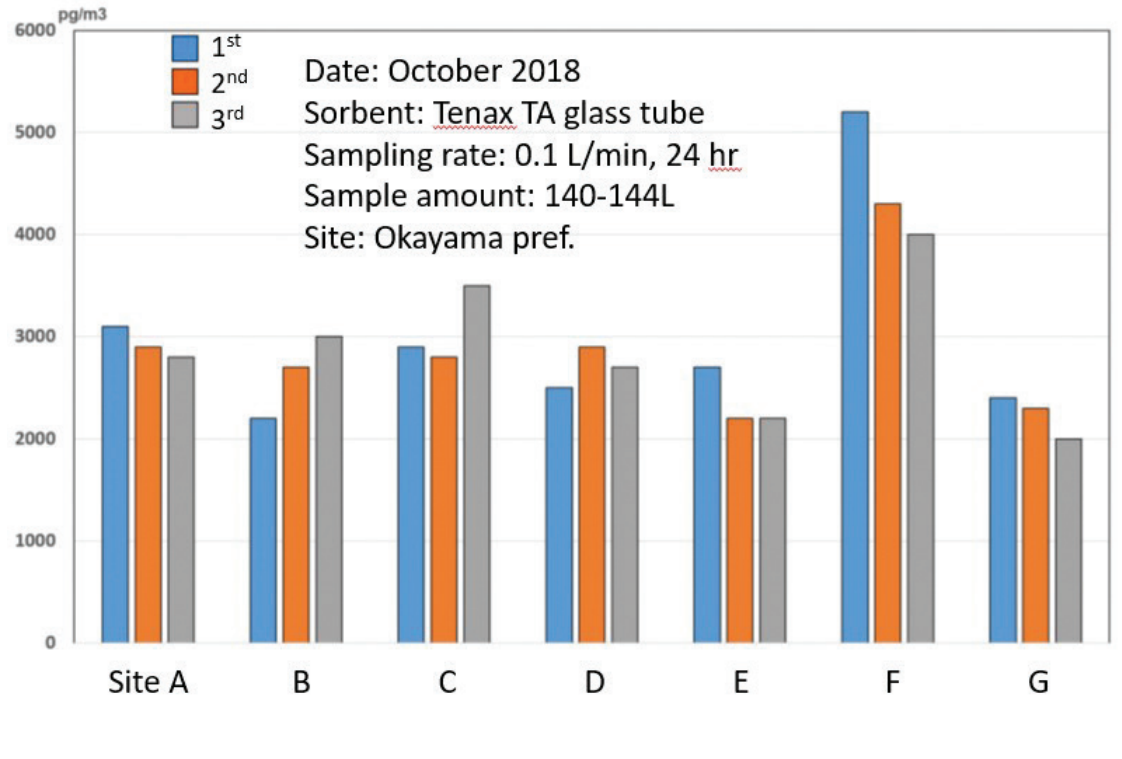


Changes of concentration ratios of OCPs isomers in Jeju (‘09~’17)



Highlight Slides, JAPAN





1. Sampling of PFAS Precursors

Low volume air sampler with 100L/min for 1week

2. Extraction

Soxhlet with acetone/ethyl acetate

3. Cleanup

Column cleanup with ENVI-carb

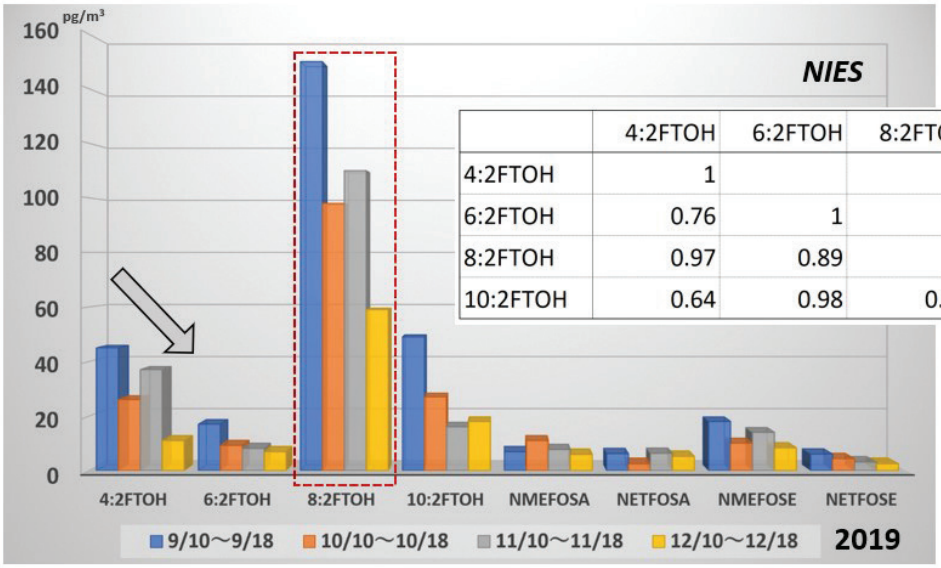
4. Measurement

GC/QMS with SIM based on PCI

Column: SUPELCOWAX (60m, 0.25mm, 0.25um)

Recovery range: 41-64 %

DL: 1.5-3.8 pg/m^3



	4:2FTOH	6:2FTOH	8:2FTOH	10:2FTOH
4:2FTOH	1			
6:2FTOH	0.76	1		
8:2FTOH	0.97	0.89	1	
10:2FTOH	0.64	0.98	0.79	1

VI–4 <2018~2020>

Cooperative research on environmental status of PPCPs in both countries

Japan - **Chisato MATSUMURA, Hiroshi YAMAMOTO, Yuki HAGA, Ryosuke YOSHIKI, Takuya KAKOI, Yuji KAWAMURA, Katsumi IWABUCHI, Toshihiro YOSHIDA**

Korea - **Jeongeun OH, Kyunghwa PARK, Kyungtae KIM**

1. Background

In recent years, it has been reported that components of pharmaceuticals and personal care products (PPCPs) have been detected from water within the environment. In addition, Environmentally Persistent Pharmaceutical Pollutants were identified as an emerging policy issue at the International Conference on Chemicals Management (ICCM4) held in October 2015, and it was agreed that international cooperation is important to promote necessary measures to address them.

Based on these circumstances, it is important to investigate the environmental status of those chemicals in order to consider the necessity of measures. Therefore, this cooperative project will aims to share experiences and information for PPCPs in both countries, including analytical methodologies and monitoring outputs within PPCPs, in the water system of the two countries.

2. Research Plan

Korea and Japan aim to conduct cooperative environmental monitoring of PPCPs to enhance their mutual expertise. The research topic includes 1) a review of monitoring and management status of PPCPs in both countries, 2) sharing analytical protocols, and 3) conducting and sharing monitoring outputs. The research is expected to begin with topic 1) along with the discussion of target chemicals of the cooperative research that are feasible for both countries. Then the research will proceed to topic 2) and finally reach to the topic of 3). A detailed plan will be discussed jointly by both countries following the progress of the cooperative study.

3. Major Outcomes

<KOREA>

1) In this study, a comprehensive investigation was performed to understand the overall occurrence, relative distribution, and bioaccumulation of seven different groups of POPs, including 27 polybrominated diphenyl ethers (PBDEs), 76 polychlorinated biphenyls (PCBs), 23 organochlorine pesticides (OCPs), three hexabromocyclododecanes (HBCDs), and 13 perfluoroalkyl substances (PFASs) as legacy POPs, as well as 41 polychlorinated naphthalenes (PCNs) and 24 short-chain chlorinated paraffins (SCCPs) as emerging POPs, through monitoring of crucian carp, sediment, and river water in the freshwater system.

2) Among the targeted POPs, SCCPs were predominant in sediment and crucian carp (accounting for more than 95%), while a dominance of PFASs was observed in river water (92%).

3) Principal component analysis revealed four different groups/patterns of POPs in all media: one for PBDEs, PCBs, and OCPs, another for HBCDs and PFASs, and the two others for PCNs and SCCPs.

4) Also, sexually dimorphic growth-dependent accumulation of legacy POPs was observed in crucian carp, indicating that POPs concentration increased with increasing fish size and males recorded significantly higher levels of POPs compared to females.

The results were published in 2020 in *Environment International* (Choo et al., 2020)

<JAPAN>

1) Analytical methods for PPCPs which have been detected in the environment were developed with the aim of improving the analytical method. Hyogo-group took charge of developing analytical method of Personal Care Products mainly, and Iwate-group took charge of Pharmaceuticals mainly.

2) In 2018, the target chemicals for Hyogo-group were Benzotriazole UV stabilizers (BUVSs), Clarithromycin, Triclosan and other PPCPs, and for Iwate-group were Diclofenac, Sertraline, and Paroxetine.

3) Hyogo-group investigated the concentration level of Clarithromycin and its metabolites, De(cladinosyl) Clarithromycin and N-desmethyl-clarithromycin, in water at upstream and downstream of the sewage treatment plants using LC-MS/MS. In the sample with the highest concentration, clarithromycin and its metabolites were detected at 960 ng/L combined, which was detected in the sample after the inflow of sewage treatment plant effluent.

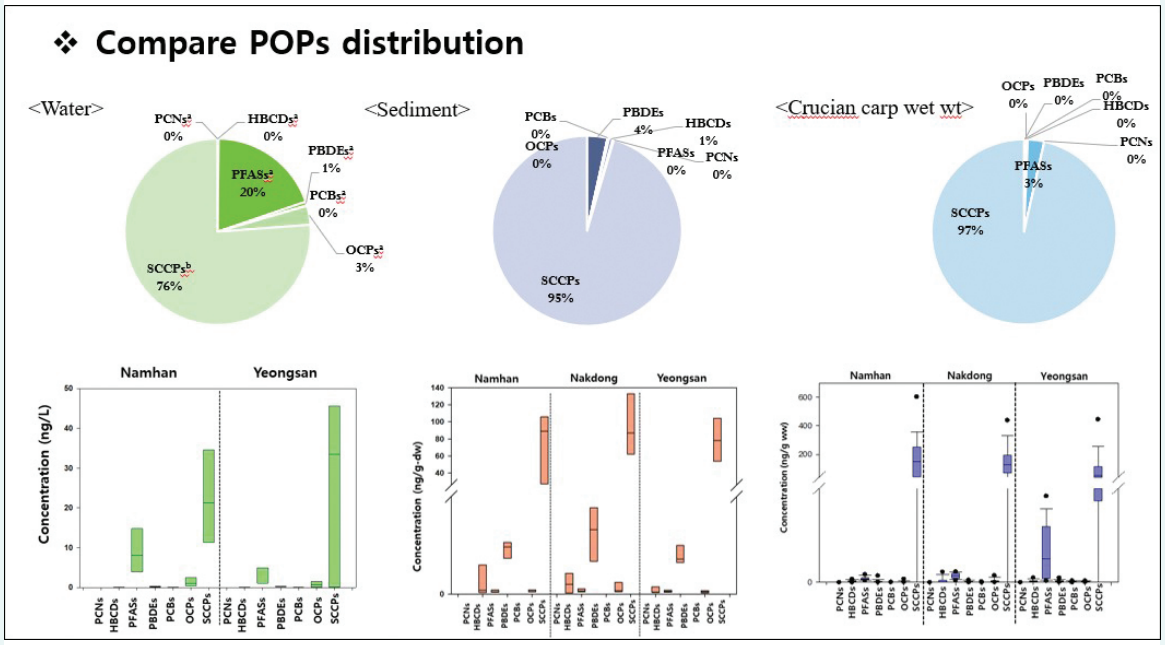
4) Iwate-group improved the method for simultaneous analysis of Diclofenac, Sertraline, and Paroxetine, and it was found to be applicable to the river water samples. It seemed that these 3 chemicals were released into the environment mainly from STP discharge water. In order to clarify whether STP discharge water is the source of these three or the other many chemicals involving PPCPs, further investigation is necessary for other rivers and STP discharge waters.

5) Hyogo-group had already investigated BUVSs in the environment (water, sediment and ambient air) using LC-MS/MS and also has developed analytical method of BUVSs in fish sample using GC-HRMS. An analytical method of BUVSs was developed in fish sample using GC-HRMS. In this study, nine species of BUVSs (UV-P, UV-9, UV-320, UV-326, UV-327, UV-328, UV-329, UV-350, and UV-234) were successfully analyzed in fish using accelerated solvent extraction (ASE), commercially available cleanup columns (without gel permeation chromatography), and GC-HRMS. Using these methods, nine samples of off Himeji, Hyogo prefecture, and 11 samples of Tokyo bay, were analyzed. The total values of BUVSs ranged from N.D. to 8.7 ng/g wet weight; these were within the range of the previously reported concentrations.

6) Iwate-group conducted comprehensive target analysis of PPCPs. River water samples were collected from two sites in June and November 2019, and August, September and December 2020, upstream and downstream of the outfall of the effluent a sewage treatment plant in Iwate and Hyogo.

7) About 500 chemicals were analyzed using LC-QTOF/MS and the differences of chemicals detected in each sample were compared. Of the 516 targeted chemicals, 88 were detected in 2019, 84 in 2020. At all site, more chemicals were detected in warm season than in cold season.

8) Confirmed the composition ratios of the detected chemicals, the highest composition ratios were pesticide (fungicide) only upstream of the sewage treatment plant in Iwate in the warm season, and PPCPs at other points and seasons. Concentrations of some chemicals exceeded the PNEC and will need to be closely monitored in the future.


❖ Compare POPs distribution
<Water>
PCNs[a] 0%
HBCDs[a] 0%
PBDEs[a] 1%
PFASs[a] 20%
PCBs[a] 0%
OCPs[a] 3%
SCCPs[b] 76%
<Sediment>
PCBs 0%
PBDEs 4%
HBCDs 1%
OCPs 0%
PFASs 0%
PCNs 0%
SCCPs 95%
<Crucian carp wet wt>
OCPs 0%
PBDEs 0%
PCBs 0%
HBCDs 0%
PCNs 0%
PFASs 3%
SCCPs 97%
Namhan
Yeongsan
Concentration (ng/L)
Namhan
Nakdong
Yeongsan
Concentration (ng/g-dw)
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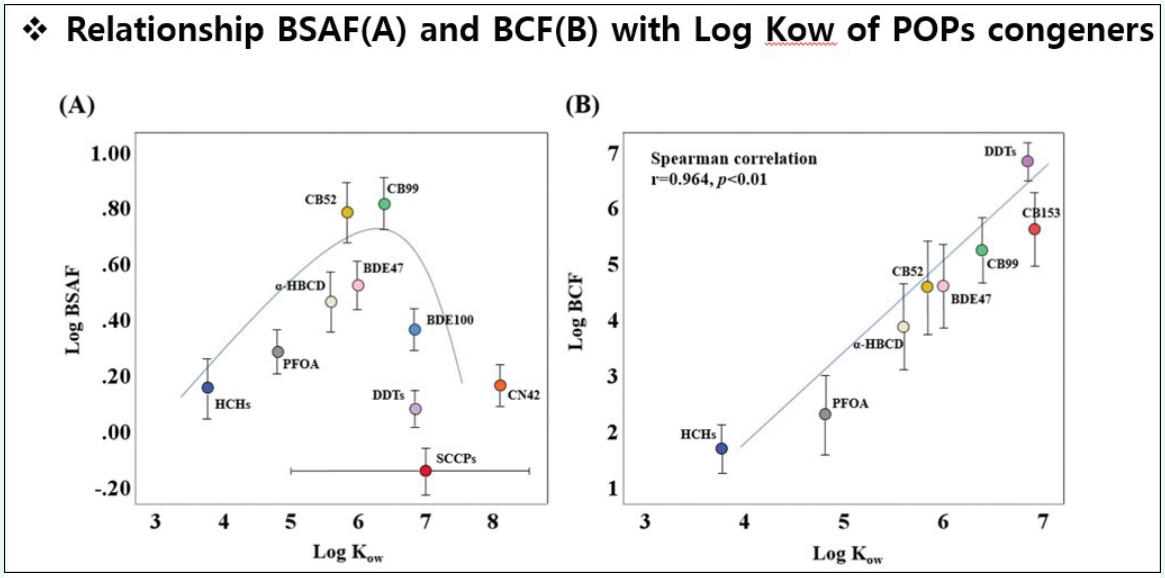
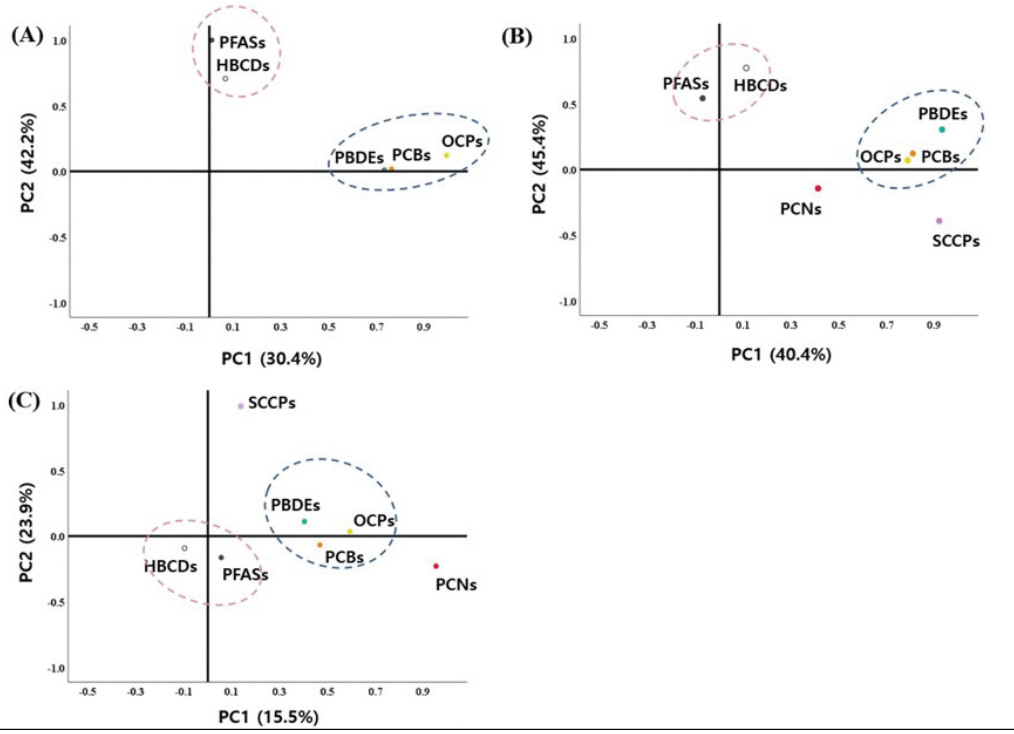
Nakdong
Yeongsan
Concentration (ng/g ww)


❖ Relationship BSAF(A) and BCF(B) with Log Kow of POPs congeners
(A)
Log BSAF
Log Kow
CB52
CB99
BDE47
α-HBCD
BDE100
PFOA
HCHs
DDTs
CN42
SCCPs
(B)
Log BCF
Log Kow
Spearman correlation
r=0.964, p<0.01
DDTs
CB153
CB99
CB52
BDE47
α-HBCD
PFOA
HCHs

❖ PCA of POPs in river water(A), sediment(B), and crucian carp(C)

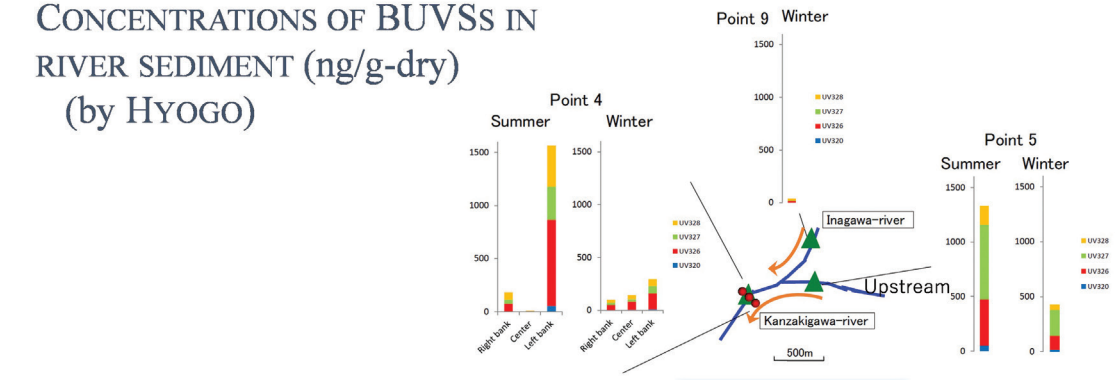


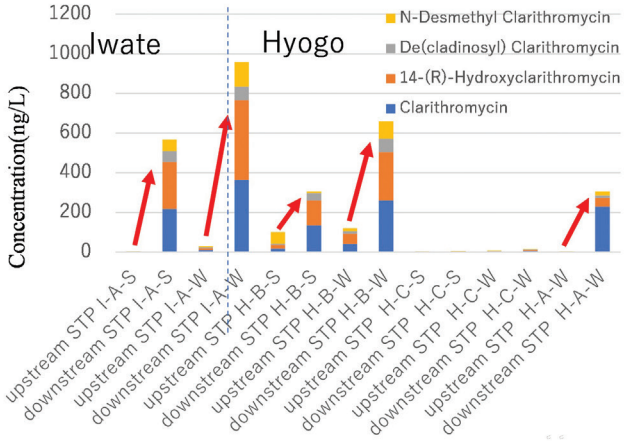
❖ POPs fish length and weight correlation

*: $p<0.05$, **: $p<0.01$

Watershed		$\sum_{41}$PCNs		$\sum_{3}$HBCDs		$\sum_{13}$PFASs		$\sum_{24}$PBDEs		$\sum_{17}$PCBs		$\sum_{12}$OCPs		$\sum_{24}$SCCPs	
		Length	Weight	Length	Weight	Length	Weight	Length	Weight	Length	Weight	Length	Weight	Length	Weight
Namhan	Wet	-0.182	-0.121	0.281	0.213	-0.151	-0.385	-0.066	-0.115	0.055	-0.185	0.497*	0.115	0.082	0.114
	Lipid	-0.403	-0.140	0.412	0.247	0.358	-0.092	0.038	-0.160	0.426	0.064	0.620**	0.245	0.171	0.386
Nakdong	Wet	-0.013	0.027	0.820**	0.743**	0.833**	0.777**	0.556*	0.700**	0.701**	0.642**	0.632*	0.652*	-0.189	-0.189
	Lipid	0.132	0.015	0.864**	0.825**	0.297	0.394	0.574*	0.697**	0.657*	0.585*	0.500	0.509	0.0903	0.101
Yeongsan	Wet	-0.031	0.252	0.436	0.680**	0.794**	0.733**	0.380	0.376	0.481	0.651**	-0.321	-0.320	-0.244	-0.229
	Lipid	0.718**	0.504*	0.214	0.536*	0.440	0.730**	-0.256	0.101	-0.081	0.487*	-0.612**	-0.350	-0.198	-0.394
3 Rivers	Wet	0.254	0.227	0.354*	0.513**	0.623**	0.567**	0.414**	0.463**	0.377**	0.449**	0.470**	0.426**	-0.179	-0.149
	Lipid	0.097	0.001	0.395**	0.483**	0.496**	0.396**	0.407**	0.441**	0.414**	0.424**	0.336*	0.260	-0.0658	-0.0447

Concentrations of BUVSs in river sediment (ng/g-dry) (by Hyogo)





Measurement of river water samples

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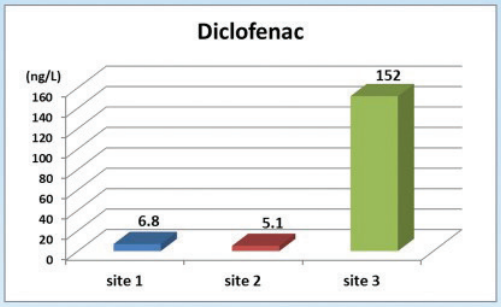
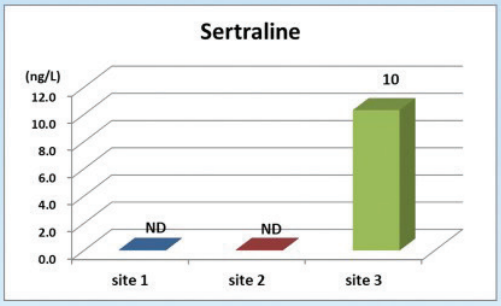
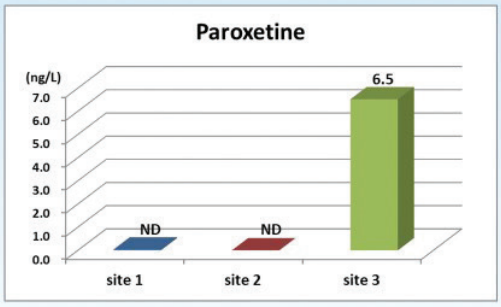
Results of analysis (Iwate, 2018)







- Diclofenac was detected in all samples.
- Sertraline and Paroxetine were detected only from the samples collected at site 3.
- Concentrations of these chemicals detected at site 3 were a little higher compared to the MOE report.

site 1 Approximately 2km upstream of the STP discharge water inflow point.
site 2 Approximately 400m upstream of the STP discharge water inflow point.
site 3 Approximately 20m downstream of the STP discharge water inflow point.
(There is no inflow between site2 and the STP discharge water inflow point.)

2019 Concentration of BUVSs in sea bass samples (ng/g-wet)

	UV-P	UV-320	UV-326	UV-327	UV-328	UV-9	UV-329	UV-234	ΣBUVSs
Sea bass 1	<4.0	<0.13	<2.0	1.2	<1.6	<0.85	0.47	<0.73	1.6
Sea bass 2	<4.0	1.5	<2.0	3.1	4.9	0.91	0.87	<0.73	11
Sea bass 3	41	<0.13	<2.0	1.0	<1.6	<0.85	0.81	<0.73	43
Sea bass 4	<4.0	2.1	<2.0	4.2	4.3	<0.85	0.45	<0.73	11
Sea bass 5	<4.0	<0.13	<2.0	1.1	<1.6	<0.85	0.52	<0.73	1.6
MDL	4.0	0.13	2.0	0.45	1.6	0.85	0.37	0.73	

Sampling point ;
Off Himeji, Hyogo prefecture

The sea bass (n=5) in off himeji were analyzed.
UV-326 and UV-234 were not detected.
UV-P, UV-320, UV-327, UV-328, UV-9 and UV-329 were detected.
UV-327 and UV-329 were detected from all samples.

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Result : Detected chemicals (Iwate, 2020)

	Target	detection	Warm Season				Cold Season			
			I-1	I-2	H-1	H-2	I-1	I-2	H-1	H-2
Pharmaceutical	162	47	3	***36***	***22***	***34***	***4***	***34***	***15***	***28***
Personal Care Product	6	3	0	3	1	2	0	2	1	1
Pesticide_herbicide	99	6	2	2	3	2	1	1	1	2
Pesticide_fungicide	88	13	***6***	6	8	7	2	2	2	2
Pesticide_insecticide	107	6	2	1	3	1	2	1	1	0
Pesticide_other use	5	0	0	0	0	0	0	0	0	0
Indusrial chemical	7	0	0	0	0	0	0	0	0	0
Others	42	9	0	5	4	5	3	3	3	6
Total	516	84	13	53	41	51	12	43	23	39

- In this study, 84 of 516 chemicals were detected.
- The number of detected chemicals at I-2 and H-2 were more than I-1 and H-1 in each season.
- Pesticides (fungicides) were most detected in I-1 during the warm season, and pharmaceuticals were most detected in other seasons and sites.
- At all site, more chemicals were detected in warm season than in cold season.
- Compared after the inflow of sewage discharge water, the types of detected chemicals showed the same tendency for both I-2 and H-2.

site I-1 (Iwate) Approximately 400m upstream of the STP discharge water inflow point.
site I-2 (Iwate) Approximately 20m downstream of the STP discharge water inflow point.
(There is no inflow between site I-1 and the STP discharge water inflow point.)
site H-1 (Hyogo) Approximately 600 m upstream from the outfall of the STP effluent.
site H-2 (Hyogo) Approximately 1 km downstream from the outfall of the STP effluent.
(One river merges between site H-1 and H-2.)

VII-1 < 2021~2022>

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

Korea - Jaeseon PARK, Saeyun KWON, Minseob KIM
Japan - Akane YAMAKAWA, Yasuyuki SHIBATA

1. Background

The UNEP Minamata Convention on Mercury emphasizes securing monitoring technology and establishing a database to identify long-distance movements of mercury in the atmosphere. Currently, there are various sources of atmospheric mercury emissions in Korea, but it is speculated that much sources are transported from long-distances, illustrating the urgency to identify the origin of pollutants.

Until now, various studies on the analysis Hg concentration in the atmosphere, such as passive samplers and mercury analysis by collecting total gaseous mercury (TGM), had been conducted, but analysis techniques based solely on simple concentrations have limitations for identifying pollutants.

Mercury stable isotopes have the advantage of obtaining information on the sources and biogeochemical processes through fractionation called MDF (Mass Dependent Fractionation) and MIF (Mass Independent Fractionation). In Korea, the foundation for the method of analysis on mercury stable isotopes by collecting TGM has been established according to the National Institute of Environmental Sciences' stable isotope research roadmap.

According to existing literature, gaseous mercury in the atmosphere is absorbed into the leaves via stomata and transferred to soil via litterfall. This shows the potential for leaves to be used as an indicator for the identification for the regional atmospheric mercury pollutants. However, to select the effective monitoring indicators for tracking atmospheric mercury pollutants and the characterization of mercury sources, the evaluation of potential isotopic fractionation across forest media should be preceded.

2. Research Plan

1) This study attempted to identify mercury concentrations and mercury stable isotope ratios in environmental media collected from various forest areas for three years, and to understand the fractionation of the mercury stable isotopes across the forest media.

2) The sampling point was selected based on proximity to Hg emissions sources and divided into western (Ganghwa-do Manisan (2020, 2021), Seosan-si Gayasan (2021), Dangjin-si Seokmun-san (2022), and eastern sides (Hambaek Mountain (2021, Jeongseon-si), Bonghwa-gun (2022), and Pohang-si Bihak-san (2020, 2021).

3) In addition, inland site (Jiri Jeongryeongchi (2021) was selected as a point where the sources of mercury in the atmosphere were considered to be relatively small, with no artificial pollutants within a radius of 50km.

4) For the accuracy of the Hg isotope values, reference materials of pine needles were developed by NIES.

3. Major Outcomes

<KOREA>

1) The concentrations of TGM displayed significant seasonal fluctuations. TGM's isotope ratio showed a high Δ^{199}Hg with dominant anthropogenic effects during the day regardless of season. MIF value Δ^{200}Hg, which has been used as an indicator for Hg^{2+}, shows the presence of anthropogenic Hg^{2+} emissions during the daytime. The comparison of the mercury stable isotope ratio in the leaves and the TGM stable isotope ratio shows two main phenomena. The first is the significant MDF caused by Hg^0 uptake by foliage. The second is the Hg^0 re-emission in the leaf, which increases the value of Δ^{199}Hg of mercury in the atmosphere by +0.45 ‰. Our results suggest small differences in Δ^{199}Hg, indicating little Hg^0 re-emission from the leaves. The magnitude of MDF occurring via Hg^0 uptake by foliage vary between −2.40 ‰ and -2.47 ‰, which was similar to previous studies.

2) In the second year, TGM, leaves, and litter were collected in the summer at the top altitude of the five forest areas distributed in various regions in Korea. Consistent with the year 2020, the δ^{202}Hg and Δ^{199}Hg values of TGM showed negative and positive values, respectively, reflecting anthropogenic Hg sources. In addition, the Δ^{200}Hg displayed indication of anthropogenic Hg^{2+} emissions impacting all five forest mountains. In regards to the MDF and MIF caused by foliar Hg^0 uptake, we observed -1.67±0.76 ‰ and 0.13±0.23 ‰ differences between foliage and TGM, respectively (Figure 4). Unlike the previous year in which the Δ^{199}Hg values of leaves and TGM matched, significant anthropogenic emissions of Hg^{2+} and deposition to foliage surfaces appear to cause Δ^{199}Hg difference. The relatively small MDF may also be owing to the anthropogenic Hg emission sources having much lower δ^{202}Hg values. Finally, when comparing mercury stable isotopes of tree leaves and litter, we observed no statistically significant differences. This means that mercury fixated within the leaves are efficiently integrated into the forest floor.

3) In the third year, TGM, leaves, and litter were collected and analyzed at the top altitude of the four forest areas in the summer. The forest areas selected in this study were Gaya, Hambaek, and Seokmun, with the last site receiving substantial amount of anthropogenic Hg. In contrary to previous years, however, the TGM isotope ratios show little sign of anthropogenic Hg^{2+} emission sources. Moreover, in the absence of anthropogenic Hg sources, the MDF reflecting Hg^0 uptake by foliage (-2.81±0.88 ‰) were more consistent with the prior studies in remote forests in the U.S. and China. Overall, our three year monitoring indicates that the presence of local anthropogenic Hg^{2+} emissions have measurable effect in governing the magnitude of δ^{202}Hg difference between the leave and TGM. Identifying the isotopic endmember for anthropogenic Hg sources would enable more effective use of foliage as a bioindicator in the future.

<JAPAN>

1) At NIES, a pretreatment method of low Hg concentration samples for Hg isotope

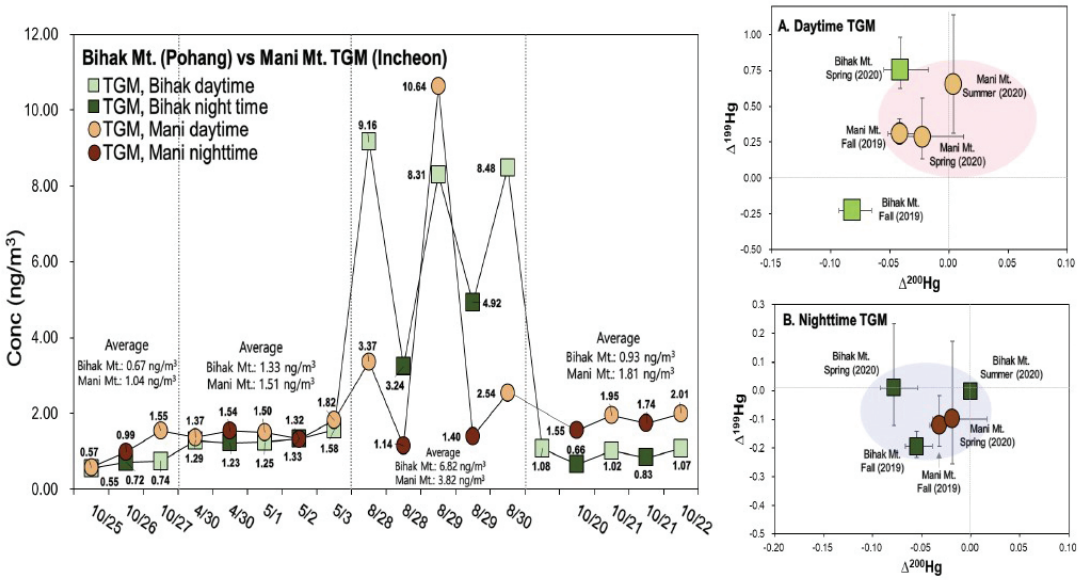
analysis using a double-furnace was developed. The heating method of the plant sample was studied using a reference material (RM) and fixed a setting where the measured Hg isotopic composition was consistent with literature values.

2) To develop a RM for pine needles with assigned reference values for total Hg concentration and Hg isotopic compositions as well as several heavy metal elements, pine needles were collected in the NIES.

3) The samples were dried, crushed, sieved, bottled, sterilized, labeled, and measured for total Hg concentration and Hg isotope compositions in accordance with ISO Guide 35.

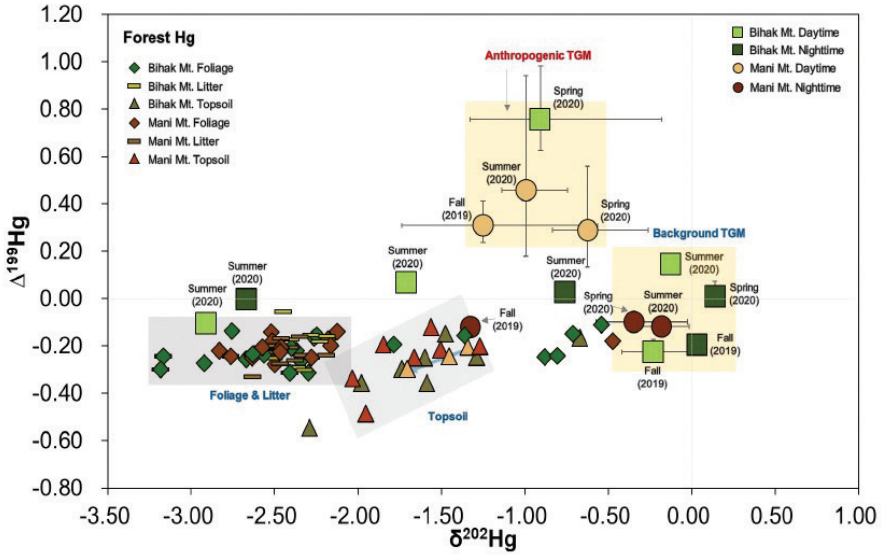
4) Pine needle RMs were collected from the same trees in 2022 and 2023. Total Hg concentrations and Hg isotopic compositions were similar. The RMs will be distributed as NIES RMs.

TGM concentration and Hg isotope



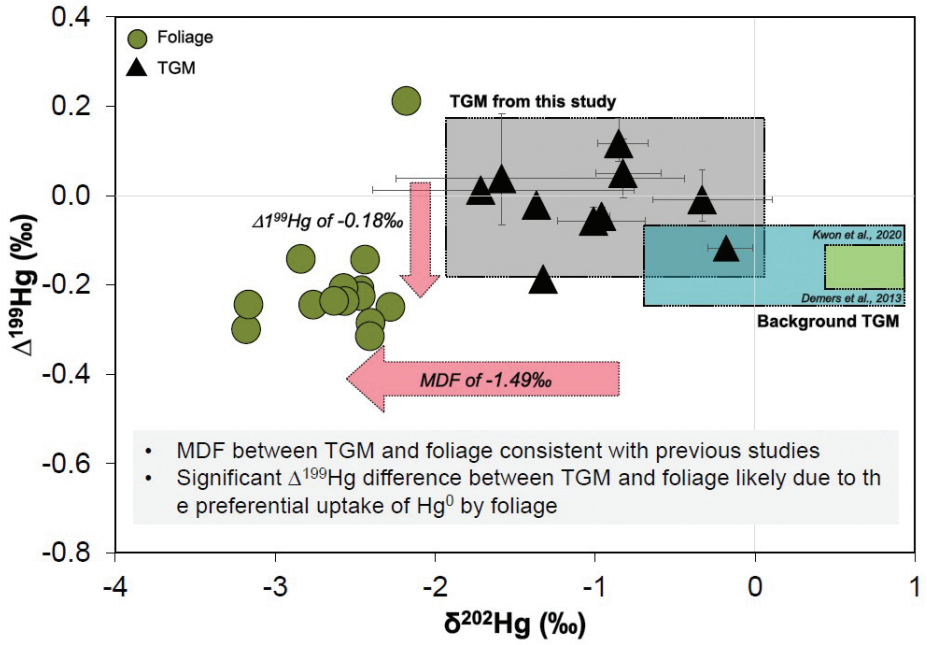
- There is a diurnal variation in TGM concentration & isotope ratios (Δ^{200}Hg, Δ^{199}Hg)
- Elevated Δ^{199}Hg during daytime reflect anthropogenically emitted Hg sources
- Low Δ^{199}Hg & Δ^{200}Hg during night time reflect long-range transport Hg

Hg isotope ratios in forest media



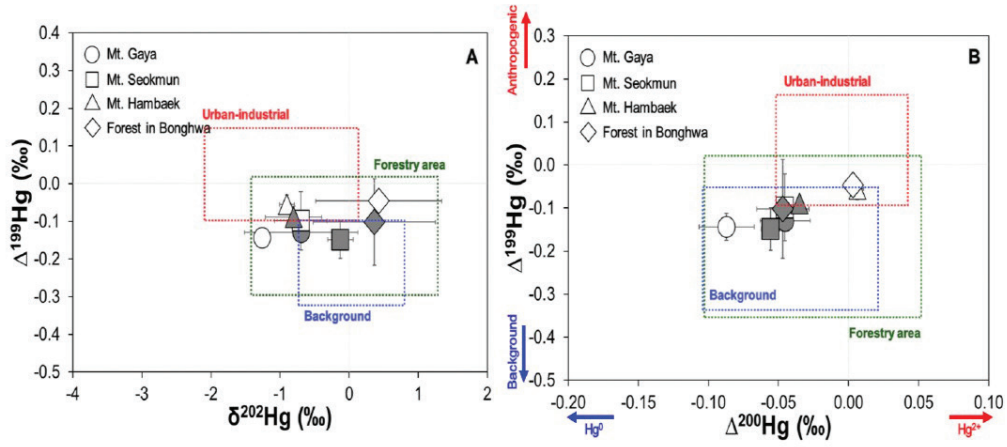
- Foliage & litter show similar Hg isotopes ratios, suggesting that atmospheric Hg has a significant influence to the forest ecosystem
- Diverse biogeochemical processes (abiotic oxidation/reduction in soil, degree of TOC binding) appear to explain the isotopic difference in soil

Comparison of Hg isotope between TGM and Foliage



- MDF between TGM and foliage consistent with previous studies
- Significant Δ^{199}Hg difference between TGM and foliage likely due to th e preferential uptake of Hg^0 by foliage

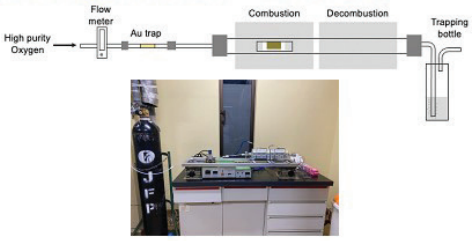
Comparison of Hg isotope between forest area and background regions



- In 2022, the isotope ratios of TGM were similar to those measured in forestry area and background regions
- Δ^{200}Hg, used to estimate Hg^{2+} proportion, and Δ^{199}Hg, used to estimate anthropogenic influences, are more consistent with background Hg^0

1. Establishing sensitivity and precision measurements of Hg isotopes for atmospheric samples

	Pretreatment (Concentration)	Sample Introduction	Measurement
Basic Method	**Both at NIES and NIER** • Acid digestion (Microwave, Hotplate) • Furnace	Plasma Ti aerosol Membrane Waste $Hg^2 \rightarrow Hg^0$	MC-ICP-MS *(Nu Plasma II)*
New Method	**A double-stage furnace – acid-trap**		MC-ICP-MS *(Nu Plasma II)*



A double-stage furnace – acid-trap protocol for the preconcentration of low Hg content samples

Basic examinations:

- **Heating step**

  Combustion furnace:
  1. ambient to 180 ℃ (12 min)
  2. held at 180 ℃ (20 min)
  3. 180 to 600 ℃ (60 min)
  4. 600 to 950 ℃ (23 min)
  5. held at 950 ℃ (30 min)
  6. cooled down from 950 to 25 ℃ (60 min)

  Decombustion furnace: 1000 ℃

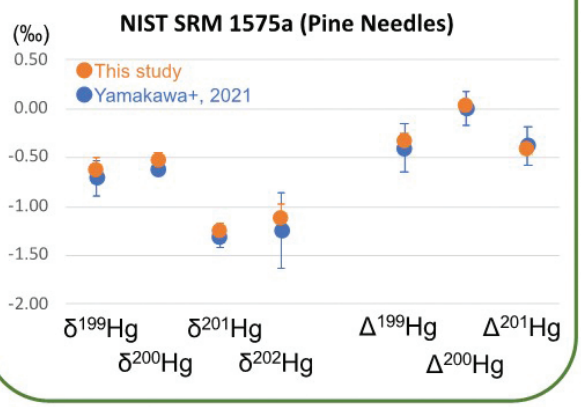
- **Acid type and concentration**

  2% $KMnO_4$ + 10% H_2SO_4 (v/v, 1:1)

Results

Recovery yield: <80%

Hg isotope: identical to reference material



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Development of Pine Needles RM for QAQC of Hg isotopic measurement

One-year pine needles were collected at two different locations (Nara and Ibaraki) to make reference materials

NIES RM Pine Needles I (Nara): 72 bottles

NIES RM Pine Needles II (NIES): 68 bottles

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Development of Pine Needles RM for QAQC of Hg isotopic measurement

Total Hg (homogeneity examined based on ISO Guide 35)

- 7 bottles were randomly selected, and 3 samples were taken from each bottle
- 21 aliquots weighing ~80 mg were analyzed for **THg** by MA-3000

	THg ppb	Uhom %
NIES RM PN I	5.48	1.06
NIES RM PN II	22.05	0.67

sufficiently homogeneous

U_{hom}: uncertainty component from batch homogeneity
moisture content: 4.3%

Hg isotopes (preliminary result)

- Developed double-stage furnace was used for pretreatment
- NIES RM Pine Needles II (sampled at Tsukuba) was measured

	δ199Hg	δ200Hg	δ201Hg	δ202Hg	Δ199Hg	Δ200Hg	Δ201Hg
NIES RM Pine Needles II (Tsukuba)	-0.83	-0.70	-1.57	-1.38	-0.48	-0.01	-0.54
	-0.81	-0.64	-1.49	-1.32	-0.48	0.03	-0.50
	-0.85	-0.74	-1.65	-1.41	-0.50	-0.03	-0.59
AVE	-0.83	-0.69	-1.57	-1.37	-0.49	0.00	-0.54
2SD (n=3)	0.04	0.10	0.16	0.09	0.02	0.05	0.09

(‰)

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VII–2 <2021~2022>

Cooperative research on the behavior and bioaccumulation of POPs-related and POPs-alternative chemicals in the aquatic environment

Japan - Takeo SAKURAI, Noriyuki SUZUKI
Korea - Hyeonseo CHO, Kyunghwa PARK, Hyunggeun PARK

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 and other related chemicals in both countries. Based on this common understanding, cooperative researches on long-range-transport modeling and bioaccumulation of these compounds had been conducted, including those with higher water solubility and various emission sources.

This cooperative research will study the occurrence, behavior, and bioaccumulation of compounds structurally similar to POPs as well as POPs alternative chemicals in the aquatic system, by experimental, field-study, and modeling approaches, and thus contribute to the understanding of the multi-medium behavior of these compounds.

2. Research Plan

1) The list of persistent organic pollutants (POPs) under the Stockholm Convention has been expanded to include 34 compounds or groups of compounds, including several perfluoroalkyl substances (PFAAs). However, there is a growing concern over POPs-related and POPs-alternative chemicals due to their structural or functional similarity to the already restricted POPs. A limited number of studies on these candidate POPs and POPs-alternative chemicals has been performed to investigate their occurrence, distribution, and bioaccumulation in the environment compared to conventional POPs. It is essential to understand the occurrence and fates of these emerging chemicals in the environment.

2) Japan and Korea will cooperatively study the bioaccumulation and occurrence of PFAAs and PFAAs-alternative chemicals in freshwater systems. The Japan side will study bioaccumulation by means of experimental or modeling methods. The Korean side will study accumulation and monitoring of PFAAs, which additionally include long-chain PFCAs (candidate POPs), and PFAA-alternative chemicals (GenX and F-53B) in Korean aquatic environment including fish.

3) Finally, both sides will evaluate the applicability of the developed model for PFAAs and PFAA-alternative chemicals in freshwater ecosystem.

3. Major Outcomes

We studied the bioaccumulation of PFAAs-alternative chemicals in freshwater systems.

The Korean side performed the field bioaccumulation monitoring of PFAAs and PFAAs-alternative chemicals, and food-web structure in aquatic ecosystem in Namhan river. Some results of bioaccumulation and biomagnification factor (BAF and BMF) through a river food web were evaluated. Most of PFAAs' BAF values (2022) in Namhan river food chain were over the bioaccumulative level (>2000 L/Kg). However, the average BAF values of Gen-X and F-53B (2021~2022) were under the bioaccumulative level. 6) Regarding BMF in predators by feeding zooplankton, the highest BMF values of PFOS were detected in Pungtungia herzi (1.49) while the highest BMF values of PFOA were detected in Goby minnow (0.16). BMF values of GenX and F-53B were detected similar values in most samples (around 1).

The Japanese side worked on modeling the bioaccumulation of PFAA-alternative chemicals with a focus on the gut uptake and depuration. The respiratory uptake efficiency, gut uptake efficiency, and depuration rate constant of PFAAs and their alternatives were parameterized by using their physicochemical properties. Then the values of these parameters of representative PFAA-alternative chemicals were predicted by using estimated physicochemical properties of these chemicals. The modeling results were preliminary discussed in the light of the field observations as well as the reported experimental results in literature.

In the future, the model predicted concentrations in fish and other aquatic animals will be compared with field measured values, and the applicability of the developed model for PFAAs and PFAA-alternative chemicals in freshwater ecosystem will be evaluated.

<KOREA>

1) PFASs concentration (2022) were detected in all species in the food-chain and ranged from 0.37~20.41 (mean 5.69) ng/g ww.

2) PFASs concentrations in Slender bittering, Korean bullhead, and Pungtungia herzi were higher considerably than other species in the food web ecosystem.

3) In terms of PFAS alternatives (2021~2022), the concentration of GenX was detected in 22/26 species and ranged from ND~1.57 (mean 0.36) ng/g ww. F-53B concentration was detected in 22/26 species and ranged from ND~0.44 (mean 0.21) ng/g ww.

4) Most of PFASs' BAF values (2022) in Yeoju food chain samples were over the bioaccumulative level (>2000 L/Kg) with high accumulation of PFOS and PFNA.

5) The bioaccumulation factor (BAF) of PFAS alternatives (GenX and F-53B) was lower than the bioaccumulative level.

6) Regarding BMF in predators by feeding zooplankton, the highest BMF values of PFOS were detected in Pungtungia herzi (1.49) while the highest BMF values of PFOA were detected in Goby minnow (0.16).

7) BMF values of GenX and F-53B were detected similar values in most samples (around 1).

8) Further studies are necessary for long-term monitoring to evaluate the accumulation of PFASs and PFAS alternatives, and the uptake pathway of these organisms is also essential to research.

<JAPAN>

1) We worked on modeling the bioaccumulation of PFAA alternatives in the aquatic food webs.

2) We developed a method to estimate respiratory uptake efficiency (αur), gut uptake efficiency (αug), and depuration rate constant (kd) of these compounds in fish.

3) The method was successfully applied to several representative PFAA alternatives.

– Preliminary evaluated with reported experimental results and the field-measured concentration ratios in Korean freshwater system.

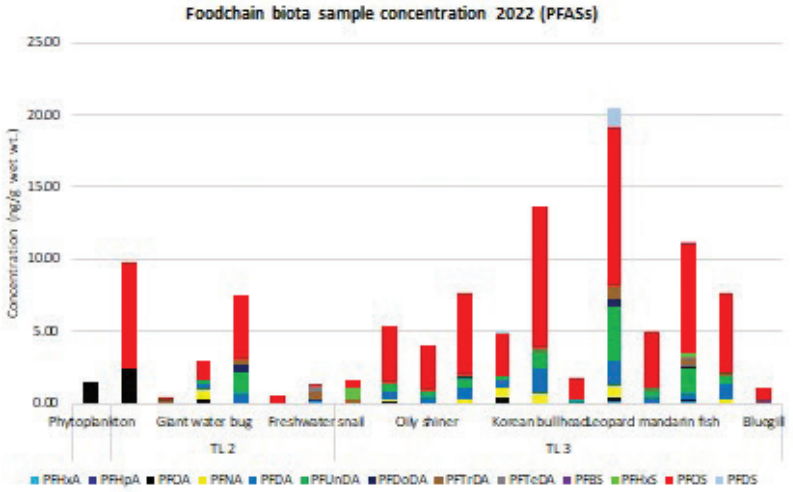
– Applicable to other alternative compounds by using computational method.

– Accuracy of the method needs further evaluation.

4) Next year, we plan to construct organism-level and food-web models, and to compare model predictions with field-measured concentration and trophic position data in Korea.

Highlight Slides, KOREA

The concentrations of PFAAs in the food chain samples in Yeoju, Korea.



Water conc.	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS
ng/L	2.30	0.41	2.48	0.16	ND	ND	ND	ND	ND	2.63	0.67	0.94	ND

- The highest PFASs concentration (ng/g ww) was 20.41 in Pungtungia herzi (돌챙이) while the lowest level PFASs was found in Catfish (메기) 0.37 ng/g ww.
- PFOS was found in almost all species (except Phytoplankton) with a range of ND~11.01 (ng/g ww)
- PFOA was found in 9/19 species with concentrations ranged from ND to 2.46 (ng/g ww)

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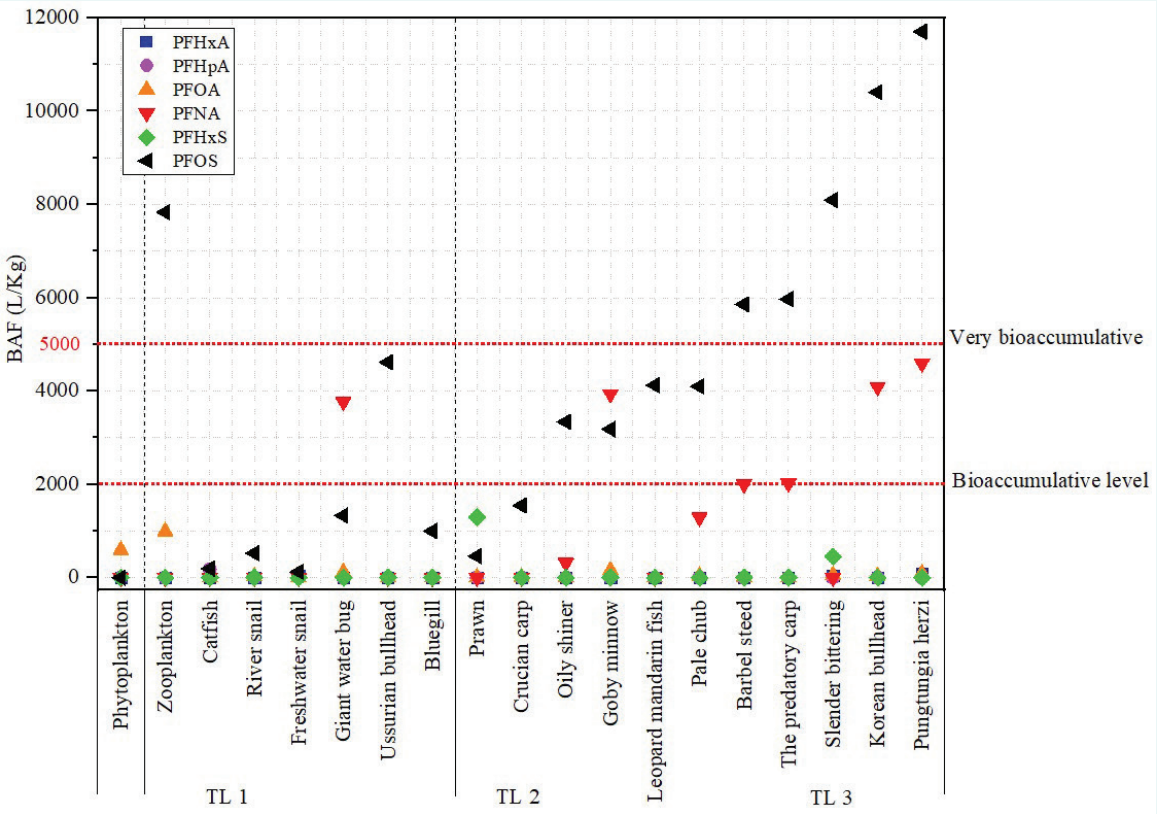
BAF levels of PFAAs in the food chain samples in Yeoju, Korea (2022)



BMF values of PFAAs in the food chain samples in Yeoju, Korea

BMF of PFAAs (2022)

Biomagnification factor (BMF) = $\frac{[PFASs]_{Predator}}{[PFASs]_{Predator's\ prey}}$

Case: Zooplankton is the predator's prey

Trophic Level	BMF	PFOA	PFOS	Other PFASs
TL2	Catfish	NA	0.02	NA
	Giant water bug	0.12	0.17	NA
	Ussurian bullhead	NA	0.59	NA
	River snail	0.03	0.07	NA
	Freshwater snail	NA	0.02	NA
TL3	Prawn	NA	0.06	NA
	Pale chub	0.04	0.52	NA
	Oily shiner	NA	0.43	NA
	The predatory carp	NA	0.76	NA
	Goby minnow	0.16	0.41	NA
	Korean bullhead	0.03	1.33	NA
	Crucian carp	NA	0.20	NA
	Pungtungia herzi	0.09	1.49	NA
	Leopard mandarin fish	NA	0.53	NA
	Slender bittering	0.06	1.03	NA
	Barbel steed	NA	0.75	NA
	Bluegill	NA	0.13	NA

Zooplankton conc.	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS
ng/g ww.	ND	ND	2.46	ND	ND	ND	ND	ND	ND	ND	ND	7.37	ND

BMF values of Alternatives in the food chain samples in Yeoju, Korea

BMF of Alternatives (2021~2022)

Case: Zooplankton is the predator's prey

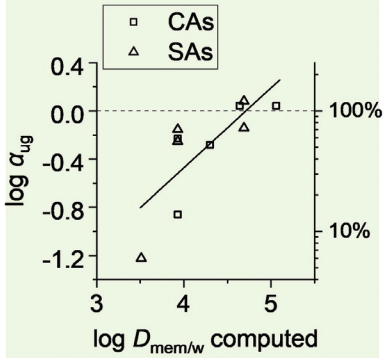
Biomagnification factor (BMF) = $\frac{[PFASs]_{Predator}}{[PFASs]_{Predator's\ prey}}$

Trophic level	BMF	GenX	F-53B
TL 2	Ussurian bullhead	NA~1.20(0.74)	NA~0.90(0.59)
	Giant water bug	NA~1.49(0.81)	NA~1.44(0.75)
	Catfish	NA~1.29(0.53)	NA~0.97(0.63)
	River snail	NA	NA
TL 3	Freshwater snail	NA~2.06(1.04)	NA~0.94(0.56)
	Micropterus salmoides	1.24	0.61
	Crab	1.46	0.99
	Eel	0.81	NA
	Cobitis tetralineata	1.35	1.16
	Gobiobotia macrocephala	NA	1.19
	Pale chub	NA~1.34(0.67)	NA~0.83(0.42)
	Crucian carp	NA~1.00(0.64)	NA~0.92(0.61)
	Oily shiner	NA	NA
	Prawn	NA~1.28(0.84)	NA~1.12(0.67)
	Opsariichthys bidens	3.61	1.16
	Slender bittering	NA~4.26(2.13)	NA~1.41(0.70)
	Goby minnow	NA~1.22(0.61)	NA~0.96(0.48)
TL 4	Pond loach	1.19	0.89
	The predatory carp	NA~1.18(0.67)	NA~0.94(0.50)
	Bluegill	NA~0.63(0.31)	NA~0.62(0.31)
	Korean bullhead	NA~0.91(0.46)	NA~0.84(0.42)
	Leopard mandarin fish	NA~1.02(0.45)	NA~0.89(0.51)
	Barbel steed	NA	NA
	Pungtungia herai	NA~1.30(0.65)	NA~0.89(0.45)

Conc. (ng/g ww)	GenX	F-53B
Zooplankton	NA~0.43(0.29)	NA~0.37(0.24)

Estimating gut uptake efficiency (α_{ug})

- We used empirical log-linear relationship for PFAAs with $D_{mem/w}$.
  - The major uptake route was assumed to be passive diffusion through cell (membranes).
  - Active transport was neglected.
  - PFOA, PFNA, PFDA, PFUnDA, PFBS, PFHxS, PFOS.
    - α_{ug}: Rainbow trout (adult[1)] and juvenile[2)]);
    - $D_{mem/w}$: computed by COSMOperm software[3)].
  - Log–log linear relationship with r = 0.77.
  - Predicted α_{ug} values >1 were treated as 1.
- Applicability to alternatives
  - $D_{mem/w}$ of alternatives may be computed
    - Good correlation (log RMSE of 0.61) reported with experimentally measured data for PFAAs and alternative compounds[3,4)].



log α_{ug} = 0.66 log $D_{mem/w}$ − 3.1

(r^2 = 0.59; n = 10;
log $D_{mem/w}$, 3.5–5.1)

1) Goeritz et al. 2013. 2) Martin et al. 2003. 3) Ebert et al. 2020. 4) Droge 2019.

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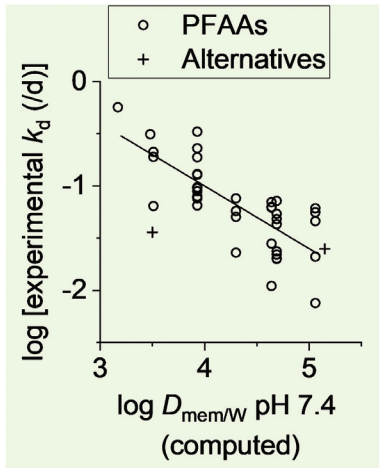
Slide presented at the 22nd Joint Symposium on POPs Research (16 February 2023)

Estimating depuration rate constant (k_d) (2)

- Empirical correlation of experimental k_d[1–11)] with $D_{mem/w}$[12,13)] provided a reasonable fit.
  - Log–log linear relationship with r = −0.76.
  - Lower correlations with D_{OW} or D_{BW}.
- Applicability to alternatives
  - $D_{mem/w}$ may be estimated with a reasonable accuracy[12,13)].



log k_d = −0.60 log$D_{mem/w}$ + 1.4

(r^2 = 0.58; n = 38;
log $D_{mem/w}$, 3.2–5.1;
Alternatives not included.)

1) Martin et al. 2003a. 2) Martin et al. 2003b. 3) Goeritz et al. 2013. 4) Sakurai et al. 2013. 5) Chen et al. 2016. 6) Qiang et al. 2016. 9) Fang et al. 2016. 10) Sun et al. 2022. 11) Zhong et al. 2022. 12) Droge 2019. 13) Ebert et al. 2020.

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Slide presented at the 22nd Joint Symposium on POPs Research (16 February 2023)

Comparison with measured and field values

- k_d available for 2 alternatives. No experimental data for α_{ug}.
  - Estimate was similar to experimental for F-53B, but much higher for GenX.

Compound	Group	k_d estimated	k_d experimental
HFPO-DA (GenX)	PFOA alt.	0.20	0.036[1*)]
6:2 Cl-PFAES (F-53B)	PFOS alt.	0.020	0.025[2*)]

* Values are uncertain because growth correction was not described. GenX value may be up to about 0.026 (= feeding rate) lower (i.e., 0.01). For F-53B feeding rate was also not available.

- BCF (k_{ur}/k_d) and BMF (k_{ug}/k_d) (10-g fish, freshwater, 20 °C, DO saturation 70%)

Compound	Group	BCF est.†	BAF field‡	BMF est.†	BMF field
HFPO-DA (GenX)	PFOA alt.	8.0	65–890 (21)$	0.017	0.29–4.3 (18)$
ADONA (DONA)	PFOA alt.	40	NA	0.21	NA
6:2 Cl-PFAES (F-53B)	PFOS alt.	1200	NA	1.2	0.14–1.9 (18)$
PFOA	PFCA	85	28–160 (7)	0.17	0.03–0.16 (7)
PFOS	PFSA	700	120–12000 (17)	0.93	0.02–1.49 (17)

† Estimates depend on ventilation or feeding rates. ‡ Excluding planktons. $ Including 2021 data.

1) Siddiqui et al. 2022. 2) Liu et al. 2020.

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Slide presented at the 22nd Joint Symposium on POPs Research (16 February 2023)

Discussion

- We worked on modeling the bioaccumulation of PFAA alternatives in the aquatic food webs.
- We developed a method to estimate gut uptake efficiency (α_{ug}) and depuration rate constant (k_d) of these compounds in fish.
- The method was successfully applied to several representative PFAA alternatives.
  - Preliminary evaluated with reported experimental results and the field-measured concentration ratios in Korean freshwater system.
  - Applicable to other alternative compounds by using computational method.
  - Accuracy of the method needs further evaluation.
- Next year, we plan
  - to construct organism-level and food-web models, and
  - to compare model predictions with field-measured concentration and trophic position data in Korea.

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Slide presented at the 22nd Joint Symposium on POPs Research (16 February 2023)

VII-3 <2021~2022>

Cooperative research on innovative monitoring technique of POPs and other priority pollutants

Japan – Yoshikatsu TAKAZAWA, Toshitaka KOGISO, Kazuhiro TOBIISHI, Shunichi NAKAYAMA, Yasuyuki SHIBATA
Korea – Hyunjeong KIM, Seam NOH

1. Background

Under the Stockholm Convention, with the initial 12 POPs listed upon adoption, further 18 toxic chemicals have been listed and then new candidates have been proposed for listing. The POPs Review Committee (POPRC) evaluates the proposals and makes recommendations to the Stockholm Convention for new candidate chemicals. Article 16 of the Stockholm Convention requires the Parties to conduct environmental monitoring of new and candidates POPs, and submit monitoring data to the Convention for the effectiveness evaluation. Japan and the Republic of Korea have been conducting harmonization and development of POPs and candidates monitoring methods in this bilateral project and will continue the project for supporting sustainable environmental monitoring program.

2. Research Plan

1) Japan and Korea will co-work to conduct inter-laboratory studies and to share analytical methods of PFAS and to compare concentration levels of PFAS in the air.

2) Japan will focus on hexafluoropropylene oxide dimer acid (HFPO-DA or GenX), which is alternative to PFOA. The validity of an analytical method will be verified and observe its airborne concentration with PFOA/PFOS/PFHxS in urban and background areas. Furthermore, given the progress of the Stockholm Convention, we will summarize information on analytical methods for benzotriazole UV stabilizers (BUVS) and proceed with preliminary air monitoring.

3) Korea will continue to improve the analytical method using LC-MS/MS and GC-MS/MS to measure neutral and ionic PFAS as much accurately as possible. Furthermore, monitoring studies will be conducted to examine the distribution of both atmospheric i- and n-PFAS in rural and urban sites.

4) In addition, we will determine a measuring method and conduct atmospheric pre-monitoring of chlorpyrifos, which is a neurotoxic pesticide in the organophosphates class of chemicals currently proposed for listing under Annex A to the Stockholm Convention.

3. Major Outcomes

<KOREA>

1) Korea conducted a monitoring study on ionic and neutral PFAS and investigated their distributional characteristics in the atmosphere based on the established analytical method

using LC-MS/MS and GC-MS/MS.

2) ΣPFSAs in urban area were observed higher than those in rural area. In summer, SC-PFCAs showed relatively high distribution ratio in both areas.

3) FTOHs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) and Et-FOSA were detected. Air concentrations of Neutral PFAS were observed relatively higher in urban area than in rural area.

4) Analytical method using GC-MS/MS for chlorpyrifos in the ambient air samples was established.

<JAPAN>

1) Analytical method for PFAS substitutes (GenX, ADONA and F-53 B) was investigated using the existing PFAS simultaneous analysis method.

2) ADONA (0.25-2.5 ng/L) was detected in some river waters. No PFAS substitutes were detected in the rainwater.

3) Air concentrations of PFAS substitutes were more than one order of magnitude lower than those of PFASs.

4) Analytical method for the determination of BUVSs using a mini-pump equipped with glass filter and PS-Air cartridge has been developed.

5) Gas adsorption characteristics differed depending on the material of the filter paper.

- Adsorption rate of gas phase: Glass < PTFE
- Total recovery: Glass < PTFE

Highlight Slides, KOREA

High-volume Air Sampling
(QFF, PUF(2ea), ACF)

700 L/min for 24hr

Soxhlet extraction
with **DCM** for 24 hr

DCM Fraction

Old POPs, CUPs Analysis

Soxhlet extraction
with **MeOH** for 24 hr

DCM Fraction → Concentrate to 0.1 mL
+ Add 1 mL MeOH Fraction, 8.9 mL H_2O

SPE (WAX cartridge)

1. **Conditioning** with
   (1) 4 mL 0.1% NH_4OH/MeOH
   (2) 4 mL MeOH
   (3) 4 mL H_2O
2. **Load the extract** dissolved in 10% MeOH/DW
3. **Washing** with
   (1) 4 mL 0.025 M Acetate buffer
   (2) 4 mL MeOH
4. **Elution** with 8 mL 0.1% NH4OH/MeOH
5. **Concentrate to 1mL**
6. **Filtration** with 0.22 μm nylon syringe filter

LC-MS/MS
(ESI negative mode)

Soxhlet extraction

High-volume Air Sampling
- QFF, ACF, PUF
- Flow rate: 700 L/min
- Collected for 24 hr (1007.9 m^3)

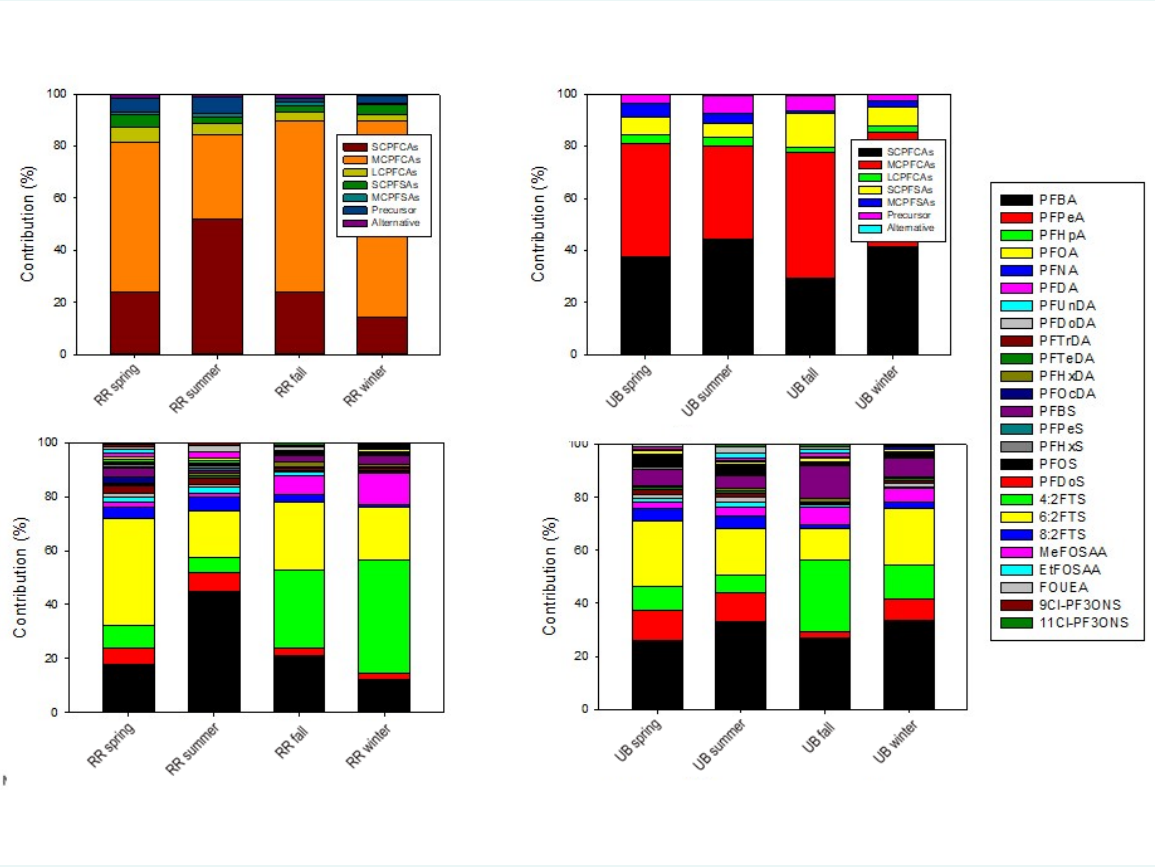
Soxhlet extraction
with DCM (500 mL) for 24 hr

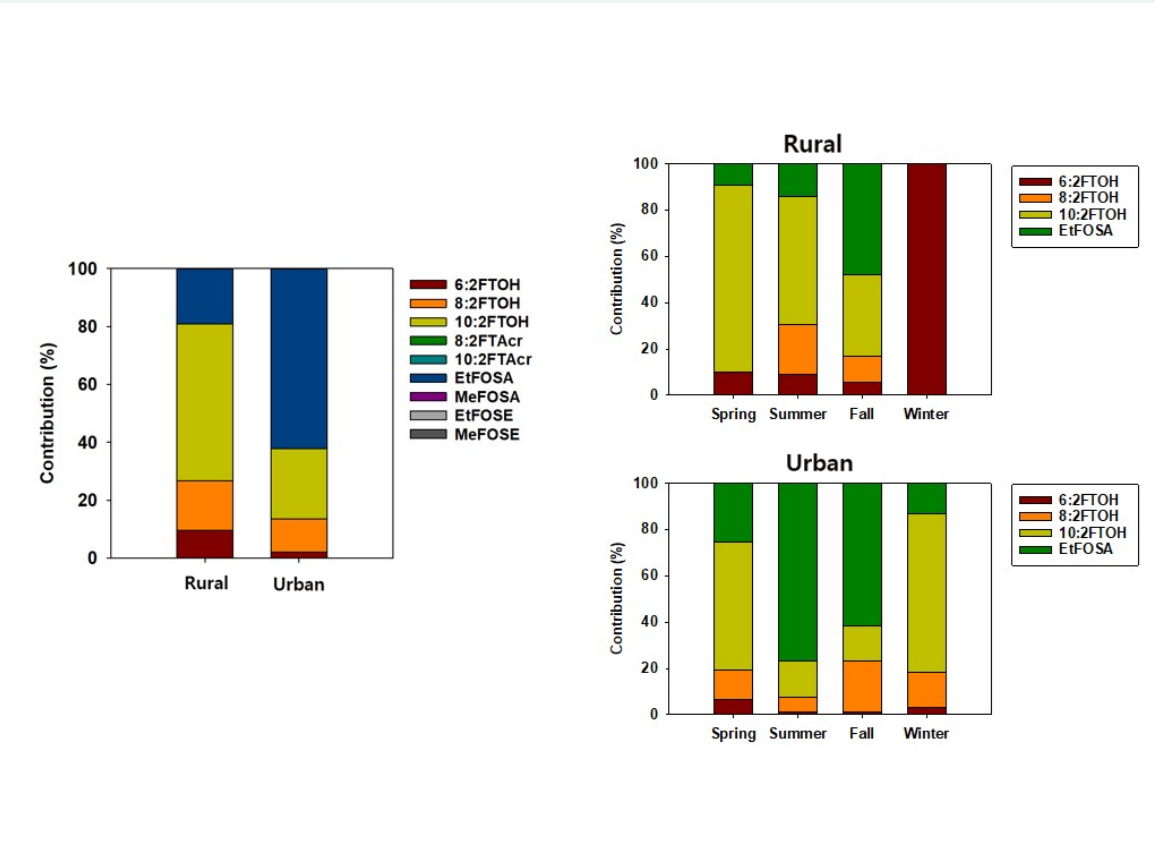
N_2 concentration
- Clean-up STD
- Concentrate to 1 mL

Clean-up
(ENVI-Carb SPE cartridge)
- Conditioning : ethyl acetate, 3 mL
- Sample loading
- Elution : ethyl acetate, 4 mL

N_2 concentration
- Internal STD
- Make up with ethyl acetate (100 μl)

GC-MS/MS (EI mode)

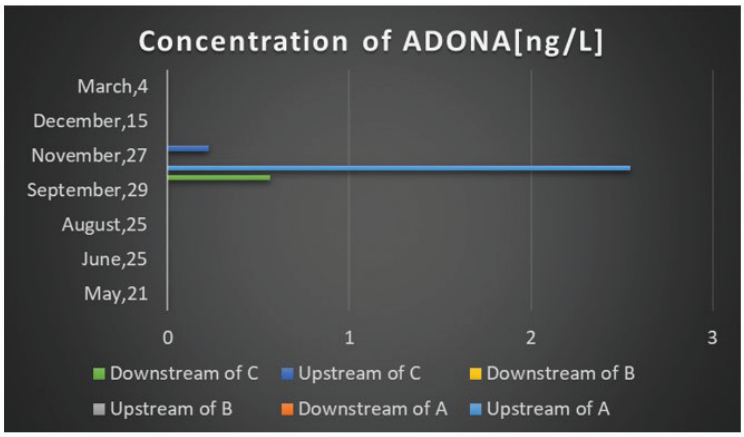

Contribution (%)
RR spring
RR summer
RR fall
RR winter
UB spring
UB summer
UB fall
UB winter
SCPFCAs
MCPFCAs
LCPFCAs
SCPFSAs
MCPFSAs
Precursor
Alternative
PFBA
PFPeA
PFHpA
PFOA
PFNA
PFDA
PFUnDA
PFDoDA
PFTrDA
PFTeDA
PFHxDA
PFOcDA
PFBS
PFPeS
PFHxS
PFOS
PFDoS
4:2FTS
6:2FTS
8:2FTS
MeFOSAA
EtFOSAA
FOUEA
9Cl-PF3ONS
11Cl-PF3ONS


Contribution (%)
Rural
Urban
6:2FTOH
8:2FTOH
10:2FTOH
8:2FTAcr
10:2FTAcr
EtFOSA
MeFOSA
EtFOSE
MeFOSE
Spring
Summer
Fall
Winter

Highlight Slides, JAPAN

River Water

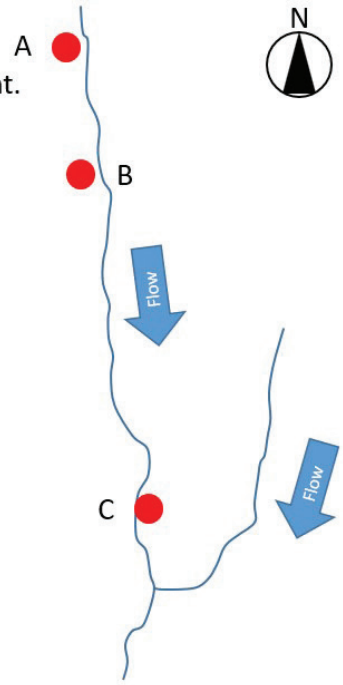
- GenX and F-53B were not detected at all in the 100x enrichment.
- Only ADONA was detected in September and November.
- The locations where ADONA was detected were different.



Rainwater

- All were not detected at all at 1000x enrichment.

Kanagawa Prefectural Government



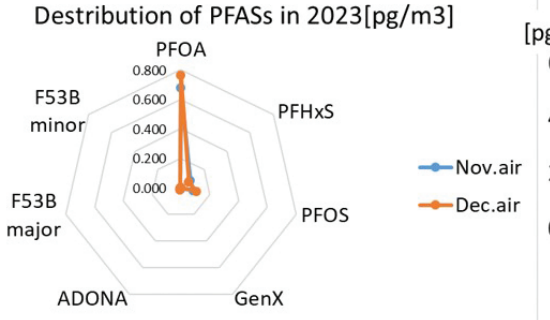
Sakai River

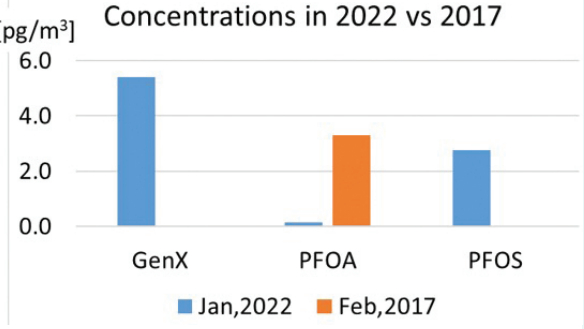
Air

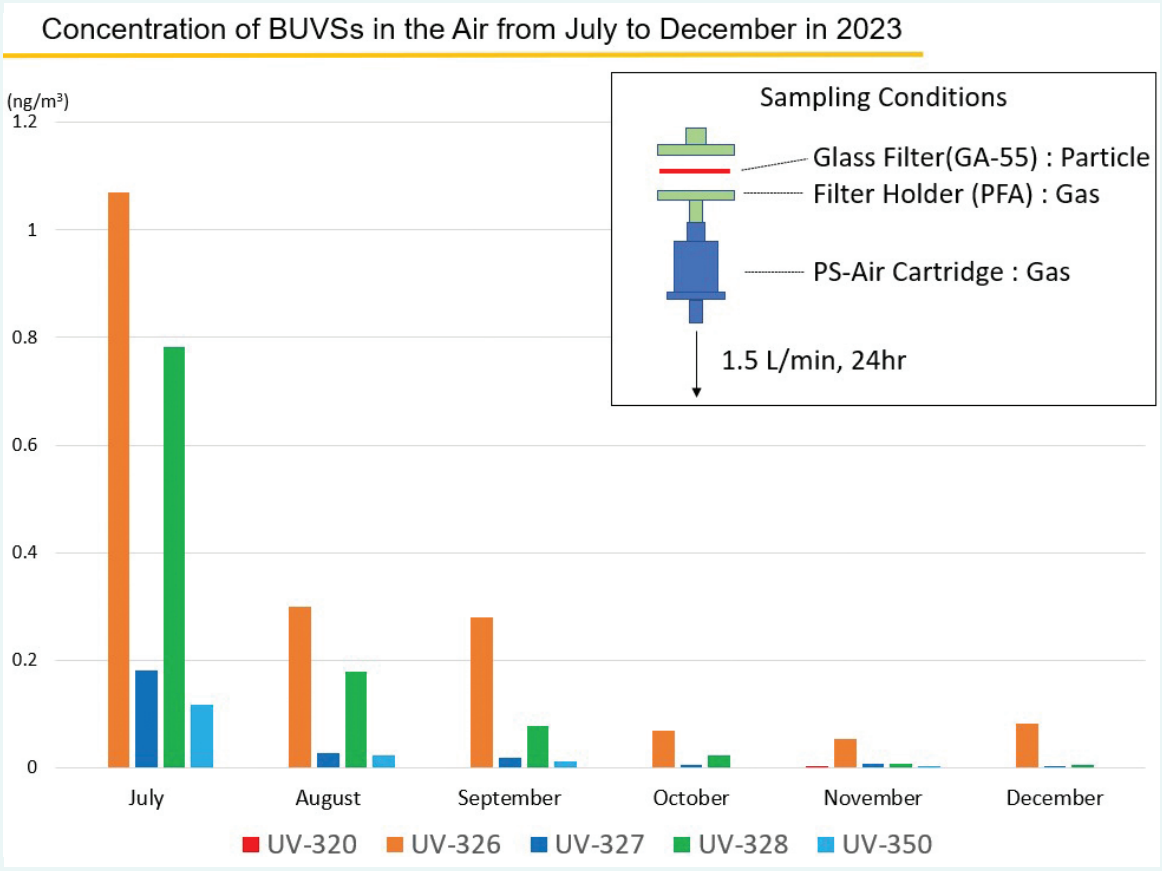
- Atmospheric concentrations of PFASs were similar to last year's results.
- Air concentrations of PFAS substitutes were more than one order of magnitude lower than those of PFASs.

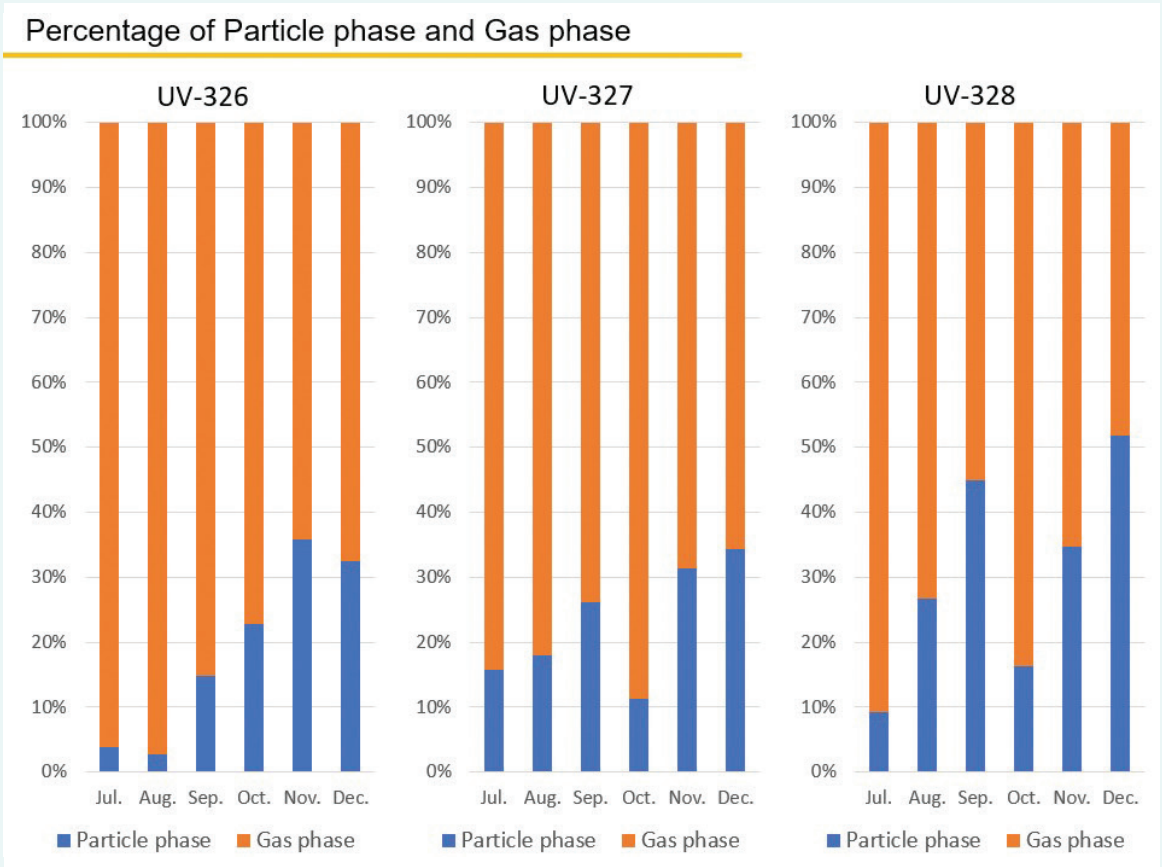
	PFOA	PFHxS	PFOS	GenX	ADONA	F53B major	F53B minor
Nov.air	0.678	0.080	0.085	0.000	0.010	0.005	0.005
Dec.air	0.767	0.067	0.106	0.000	0.014	0.006	0.005

[pg/m^3]






Concentration of BUVSs in the Air from July to December in 2023
(ng/m³)
1.2
1
0.8
0.6
0.4
0.2
0
July
August
September
October
November
December
UV-320
UV-326
UV-327
UV-328
UV-350
Sampling Conditions
Glass Filter(GA-55) : Particle
Filter Holder (PFA) : Gas
PS-Air Cartridge : Gas
1.5 L/min, 24hr


Percentage of Particle phase and Gas phase
UV-326
UV-327
UV-328
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Jul.
Aug.
Sep.
Oct.
Nov.
Dec.
Particle phase
Gas phase

VII-4 <2021~2022>

Cooperative research on the monitoring of Contaminants of Emerging Concern (CECs) in the environment

Japan - Hiroshi YAMAMOTO, Chisato MATSUMURA, Kazumasa SAKAMOTO, Takuya KAKOI, Hitomi HASEGAWA, Takahiro NISHINO, Mika KATO, Ruriko TAHARA, Shinichiro NAGAHORA
Korea - Jeongeun OH, Kyunghwa PARK, Kyungtae KIM, Byeongwoo LEE

1. Background

In recent years, the frequent and ubiquitous detection of pharmaceuticals and personal care products (PPCPs) in the water environment has been reported by many countries. Due to their potential of toxicity and adverse effects on the aquatic environment, PPCPs are now regarded as contaminants of emerging concerns (CECs) and are receiving a significant social attention these days. Therefore, understanding the status of CECs contamination in the water environment is strongly needed to manage and control these chemicals, but there is no agreement or standardized method to analyze CECs worldwide so far.

Based on these circumstances, this cooperative research between Japan and Korea was planned to develop an analytical method for CECs like PPCPs by sharing their experiences and know-how for analysis. In addition, the monitoring of CECs in the water system of the two countries will be conducted and the results will be also be shared.

2. Research Plan

1) Korea and Japan will conduct a cooperative project on environmental monitoring of CECs to enhance their analytical and research capabilities with each other. The research topics includes 1) a comprehensive review of the monitoring and management status of CECs in both countries, 2) sharing analytical protocols, and 3) conducting and sharing monitoring outputs.

2) In Japan, PPCPs such as pharmaceuticals (clarithromycin and its metabolites), benzotriazole UV stabilizers (BUVSs), phosphate ester flame retardants (PFRs) and artificial fragrance compounds will be investigated in water, sediment and fish samples (Hokkaido, Tokyo, Kanagawa, Nagoya, Hyogo, Fukuoka). In addition, simultaneous analysis will be regularly conducted upstream and downstream of sewage treatment plants.

3) In Korea, an analytical method using GC-Q-TOF/MS to detect the CECs in environmental water samples including fish will be developed. An in-house library using over 100 chemical standards will also established. With the developed analytical method and in-house library, suspect analysis will be conducted on representative river water, sediment and biota samples, and priority chemicals will be determined for future monitoring studies.

3. Major Outcomes

<KOREA>

1) In this study, sample preparation methods were proposed for suspect and non-target screening (SNTS) using gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) in the aquatic environment.

2) The pretreatment methods were evaluated based on detection rates, recoveries, and screening detection limits (SDLs) for 316 substances spiked into surface water, sediment, and biota samples. The detection rates of the spiked compounds were 92.1% and 98.7% by the sample preparation methods for water (solid-phase extraction using the HLB cartridge) and sediment (ultrasonic extraction (USE) with HLB cartridge clean-up), respectively. Similarly, USE with HLB cartridge clean-up gave the highest detection rate (87.9%) for biota samples

3) However, an additional pretreatment method using the deactivated silica gel clean-up was necessary for the detection of persistent organic pollutants (POPs). The SDL ranges of spiked compounds using the suggested pretreatment methods were 0.01–23.5 ng/L for surface water, 0.02–37.5 ng/g dry weight for sediment, and 0.01–12.2 ng/g wet weight for biota.

4) Although some pollutants, such as POPs had SDLs that were higher than the levels normally detected in the aquatic environment as reported in previous studies, the analytical methods suggested in the present study were satisfactory for the SNTS of most pollutants originating from anthropogenic sources.

5) The results were published in 2022 in the journal *Science of The Total Environment* (Sim et al., 2022).

<JAPAN>

1) Analytical methods for pharmaceuticals and personal care products (PPCPs) which have been detected in the environment were developed and environmental monitoring was conducted. The concentrations of clarithromycin, azithromycin, roxithromycin, erythromycin, its metabolites, and other pharmaceuticals in water upstream and downstream of sewage treatment plants in Hokkaido, Tokyo, Nagoya city, and Hyogo prefectures were measured using LC-MS/MS. Analysis at the ppt level has become possible. Concentrations of four phenols (phenol, cresol, 2,4-DCPh, 2,4,6-TBPh) were measured using GC/MS, while those of antibiotics and their metabolites, such as clarithromycin, and phosphorus flame retardants (PFRs) were measured using LC/MS/MS.

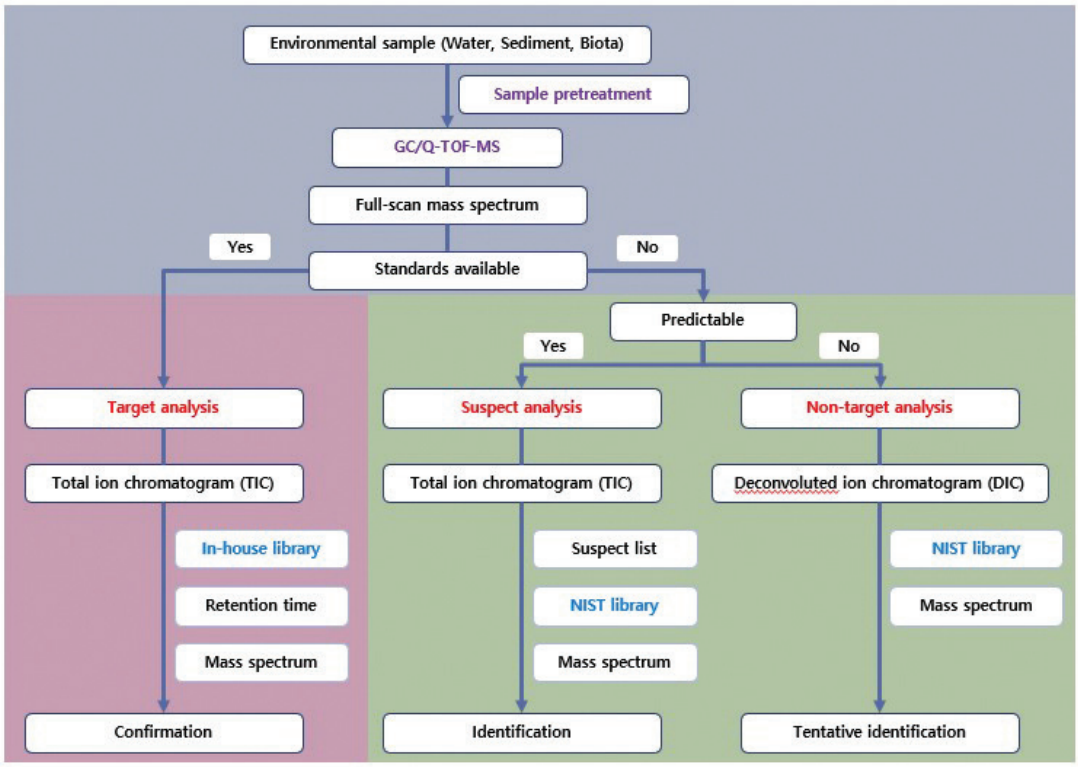
2) As a result, in phenols, phenol and 2,4-dichlorophenol were both detected in downstream and urban area with a range of ND ~ 110 ng/L. Eight congeners were detected for PFRs, with the exception of TPP. For phenols and PFRs, the detected concentrations did not exceed the predicted no effect concentrations (PNECs).

3) The selected PPCPs (antibiotics, antihypertensive agent, and caffeine etc.) were detected at ppt to ppb levels. Clarithromycin, a macrolide antibiotic, and its metabolites exceeded PNEC in some urban rivers ranging from N.D. (not detected) to 760 ng/L. Many substances showed a trend with higher concentrations in downstream of the drainage

outlets of sewage treatment plants, so the effluent from sewage treatment plants is considered to be the major source of inflow into the environment.

4) An analytical method of BUVSs was developed in fish sample using GC-HRMS. In this study, eleven species of BUVSs (UV-P, UV-9, UV-320, UV-326, UV- 327, UV-328, UV-329, UV-350, UV-234, UV-531 and UV-928) were successfully analyzed in fish using accelerated solvent extraction (ASE), commercially available cleanup columns (without gel permeation chromatography), and GC-HRMS. Using these methods, nine samples of Hyogo prefecture, Tokyo, and Hiroshima prefecture, were analyzed. The total values of BUVSs ranged from N.D. to 4.0 ng/g wet weight; these were within the range of the previously reported concentrations.

❖ Target, suspect, and non-targeted screening procedures



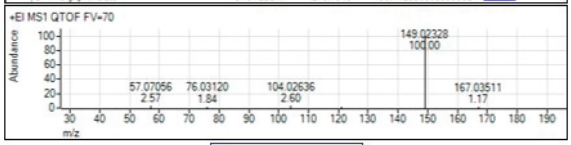
❖ Target screening to In-House Library

Target list

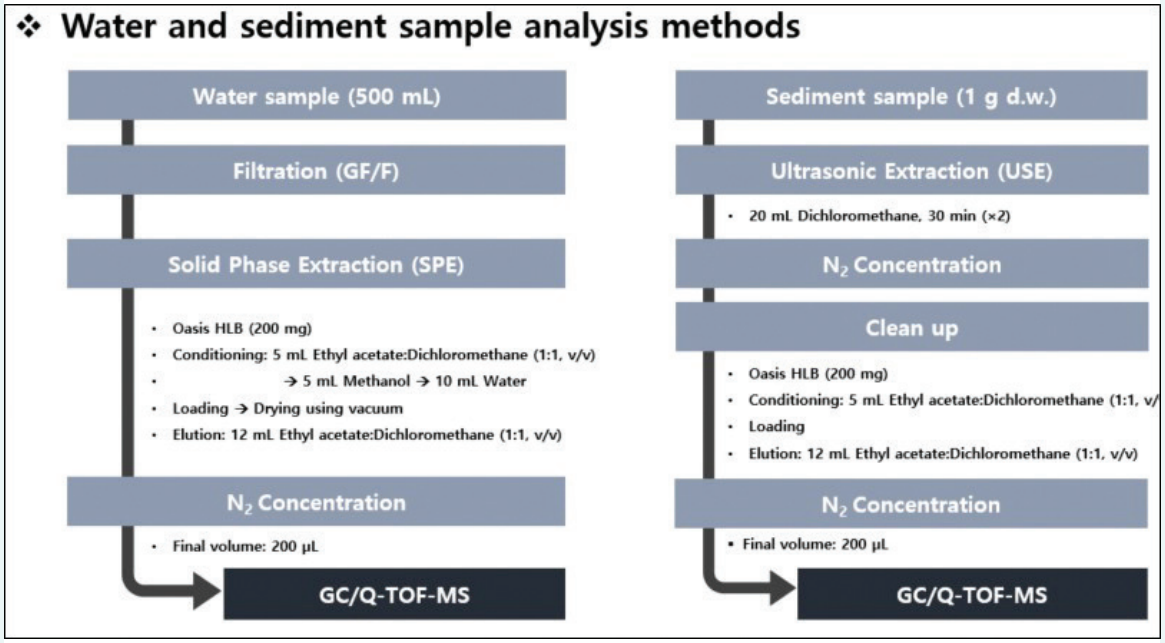
Class	Compound group
POPs	PCDD/Fs (17)
	PCNs (18)
	PCBs (62)
	PBDEs (30)
CECs	NBFRs (10)
	OPFRs (10)
	BUVs (8)
	VMSs (8)
	Plasticizers (27)
	SMCs (3)
Etc.	PAHs (16)
	Phenols (13)
	Pesticides (114)

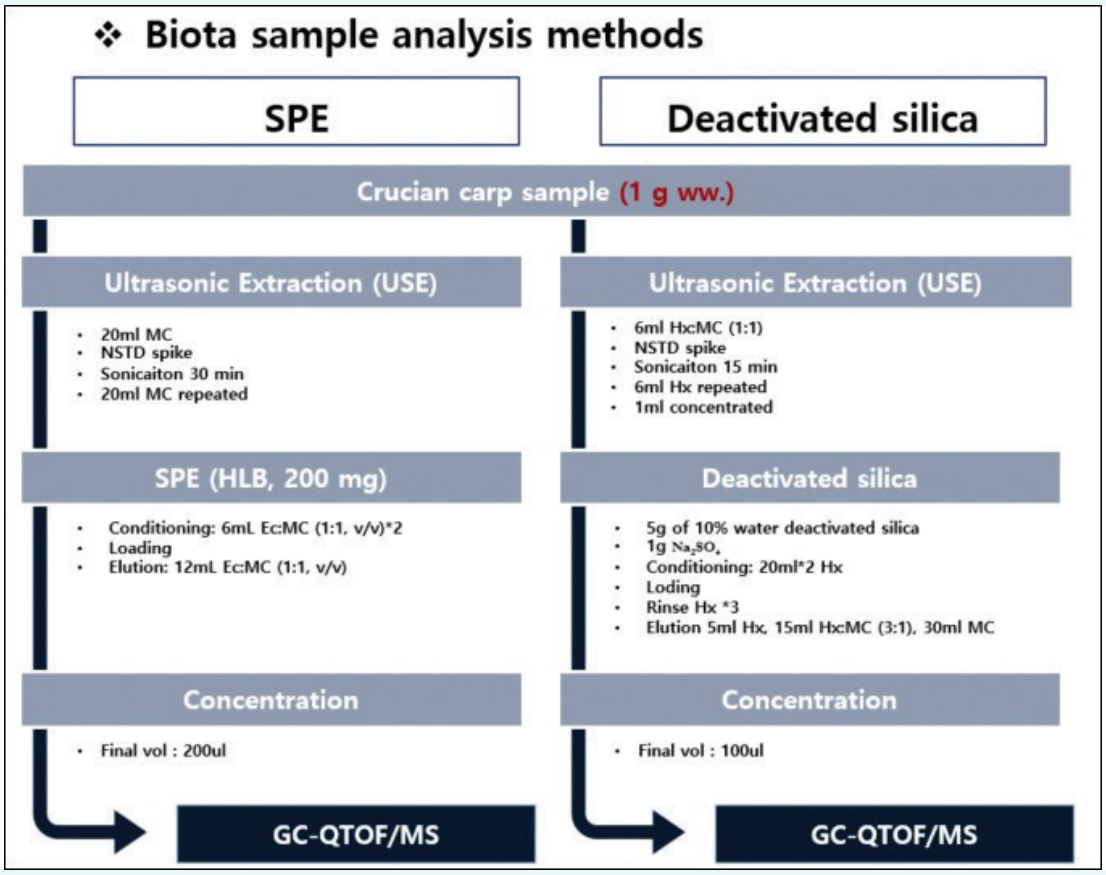
Personal Compound Database and Library (PCDL)

Name	Formula	Mass	Retention Time	CAS
Dimethyl phthalate	C10H10O4	194.05791	15.409316666666667	131-11-3
Diethyl adipate	C10H18O4	202.12051	13.89335	141-28-6
Diisobutyl phthalate	C16H22O4	278.15181	24.355233333333334	84-69-5
Dibutyl adipate (n+iso)	C14H26O4	258.18311	20.656916666666667	105-99-7
Benzyl benzoate	C14H12O2	212.08373	22.528283333333334	120-51-4
Dimethyl adipate	C8H14O4	174.08921	10.833633333333333	627-93-0
Di-n-butyl phthalate	C16H22O4	278.15181	26.24325	84-74-2
Bis(2-methoxyethyl) phthalate	C14H18O6	282.11034	26.909616666666668	117-82-8
Bis(4-methyl-2-pentyl) phthalate - isomer 1	C20H30O4	334.21441	28.297866666666668	84-63-9
Bis(4-methyl-2-pentyl) phthalate - isomer 2	C20H30O4	334.21441	28.3756	84-63-9
Bis(2-ethoxyethyl) phthalate	C16H22O6	310.14164	29.075283333333335	605-54-9
Diamyl phthalate	C18H26O4	306.18311	29.791616666666666	131-18-0
Di-n-hexyl phthalate	C16H22O4	278.15181	33.112333333333332	84-74-2



Ex) Plasticizers


❖ Water and sediment sample analysis methods
Water sample (500 mL)
Filtration (GF/F)
Solid Phase Extraction (SPE)
• Oasis HLB (200 mg)
• Conditioning: 5 mL Ethyl acetate:Dichloromethane (1:1, v/v)
→ 5 mL Methanol → 10 mL Water
• Loading → Drying using vacuum
• Elution: 12 mL Ethyl acetate:Dichloromethane (1:1, v/v)
N2 Concentration
• Final volume: 200 µL
GC/Q-TOF-MS
Sediment sample (1 g d.w.)
Ultrasonic Extraction (USE)
• 20 mL Dichloromethane, 30 min (×2)
N2 Concentration
Clean up
• Oasis HLB (200 mg)
• Conditioning: 5 mL Ethyl acetate:Dichloromethane (1:1, v/
• Loading
• Elution: 12 mL Ethyl acetate:Dichloromethane (1:1, v/v)
N2 Concentration
• Final volume: 200 µL
GC/Q-TOF-MS


❖ Biota sample analysis methods
SPE
Deactivated silica
Crucian carp sample (1 g ww.)
Ultrasonic Extraction (USE)
• 20ml MC
• NSTD spike
• Sonicaiton 30 min
• 20ml MC repeated
SPE (HLB, 200 mg)
• Conditioning: 6mL Ec:MC (1:1, v/v)*2
• Loading
• Elution: 12mL Ec:MC (1:1, v/v)
Concentration
• Final vol : 200ul
GC-QTOF/MS
Ultrasonic Extraction (USE)
• 6ml Hx:MC (1:1)
• NSTD spike
• Sonicaiton 15 min
• 6ml Hx repeated
• 1ml concentrated
Deactivated silica
• 5g of 10% water deactivated silica
• 1g Na2SO4
• Conditioning: 20ml*2 Hx
• Loding
• Rinse Hx *3
• Elution 5ml Hx, 15ml Hx:MC (3:1), 30ml MC
Concentration
• Final vol : 100ul
GC-QTOF/MS