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Global contamination of Perfluorinated Compounds ***- Recognition of their problems, countermeasures and future***

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Today's Contents

- 1. Introduction (POPs Problem)**
- 2. Perfluorinated Compounds (PFCs)**
- 3. World Distribution**
- 4. Their Sources and Effects of WTPs**
- 5. Countermeasures and Future**





POPs Problem

Introduction (POPs problem)
Perfluorinated compounds (PFCs)
World distribution
Their sources and effects of WTPs
Countermeasures and future

Persistent Organic Pollutants (POPs):

*Chemical substances that **persist** in the environment, **bioaccumulate** through the food web, and pose a **risk** of causing adverse effects to human health and the environment.*

<UNEP> <http://www.chem.unep.ch/pops/>

Three Key Properties:

- > **Persistency** : *never be reduced naturally*
(in biological and photolysis processes)
- > **Bioaccumulation** : *low concentration in discharge*
→ *high concentration in organisms*
- > **Risk** : *effects caused after long term contact*
(Toxicity recognition after a long period of usage)



POPs Contamination

Type 1: Hazardous material Discharge

Type 2: Organic Pollution

Type 3: Eutrophication

Type 4: POPs Contamination

Polluters = Victims
Merits vs. Risk

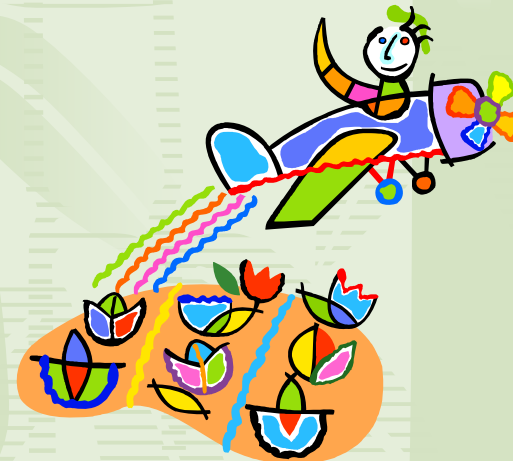
Sources: Every place (manufacturers, users, consumers)

Pollutants: POPs (Persistent organic pollutants)

Influences: Increase of long-term risk to the public
(sterility, feminization, endocrine disruption, cancer)

Range: world-wide (including arctic circle)

Measures: Ban of manufacture and use





Stockholm Convention on Persistent Organic Pollutants (POPs)

2001 May: Adoption
2004 May: Enforcement (ratification in 50 parties)
Ratification: 128 parties

A **global treaty** to protect human health and the environment from persistent organic pollutants (POPs).

To **outlaw nine*** of the "dirty dozen" chemicals\$,

To **limit the use** of **DDT** to malaria control,

To **reduce** unintentional production of **Dioxins** and **Furans**.

Parties to the convention have agreed to a process by which persistent toxic compounds can be reviewed and added to the convention, if they meet certain criteria for persistence and transboundary threat.

* Aldrin, Endrin, Heptachlor, HCB, Dieldrin, Chlordane, PCB, Toxaphenes, Mirex

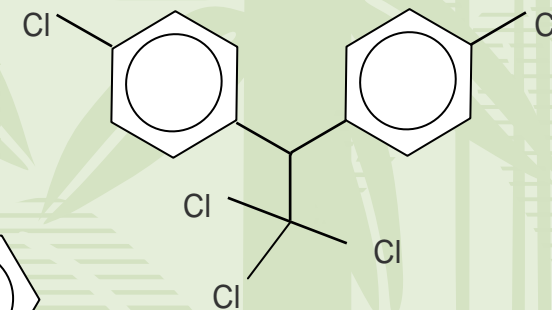
\$ nine* + DDT + Dioxins and Furans;

All of them are **Chlorinated Cyclic Hydrocarbons**

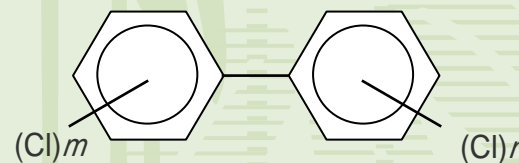


History of pollutants detected in the food-chain

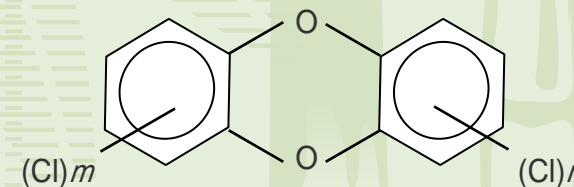
DDT 60's Rachel Carson (Silent Spring)
(Dichloro-diphenyl-trichloro-ethane,
Insecticide)



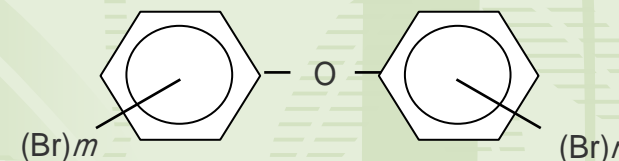
PCB 70's Soren Jensen
(Poly-chlorinated biphenyls,
Insulation oil)



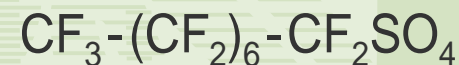
Dioxin 80's Chistoffer Rappe
(Poly-chlorinated dibenzo-dioxins,
Defoliant (Viet Nam War), Incineration by-products)



PBDE 90's Koidu Noren
(Poly-brominated diphenyl-ethers,
Fire proofing agents)



PFOS 00's 3M, John Giesy
(Perfluoro-octane sulfonate,
Water repellent)

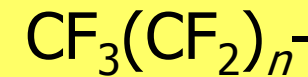




Perfluorinated Compounds (PFCs)

Introduction (POPs problem)
Perfluorinated compounds (PFCs)
World distribution
Their sources and effects of WTPs
Countermeasures and future

Synthesized fully fluorinated compound,
widely used in industrial and commercial
applications since the 1960s.

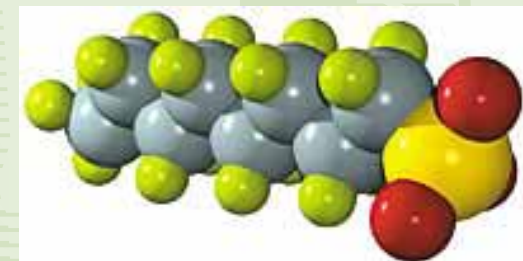


Unique Characteristics: hydrophobic & hydrophilic (oleophobic)
→ water-repellent, non-stick materials

Representative compounds

PFOS: *Perfluoro-octane Sulfonate* $\text{C}_8\text{F}_{17}\text{SO}_3^-$

PFOA: *Perfluoro-octane Acid* $\text{C}_8\text{F}_{15}\text{OO}^-$





Applications and toxicity

PFOS: *surface treatment, paper protection, performance chemical*

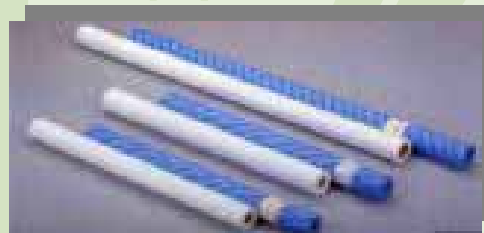
e.g. Scotchgard; Carpet; Cup & plate; Fire fighting foam;

PFOA: *intermediate, (salts:)emulsifier and surfactant*

e.g. Gore-Tex; Teflon (PTFE); Soap; Shampoo

Toxicity: *Peroxisome proliferation, Mitochondrial toxicity, Cell membrane disruption, Cancer of liver and spleen of rodents*

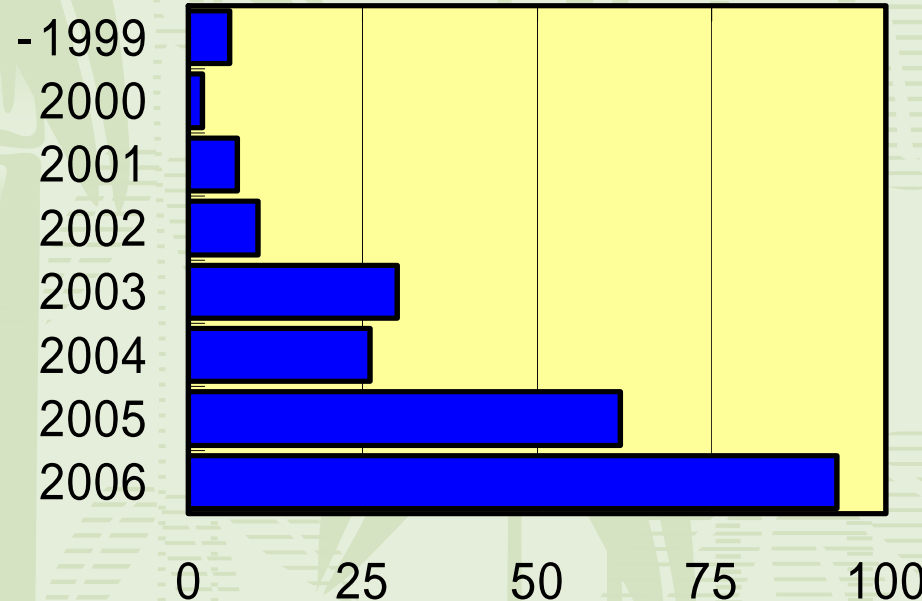
Endocrine Disrupter: *Increase estrogen and decrease testosterone Decrease thyroid hormone levels*





Study on PFOS and PFOA

Year	Content
1956	Scotchgard (PFOS contained) was invented and manufactured.
1999	High PFOS concentration were detected in the blood of laborers
2000	3M Co. phased out manufacture and use of PFOS
2002	OECD issued <i>Harzardous Assessment of PFOS and its salts</i>
2003	US EPA issued <i>Harzardous Assessment of PFOA and its salts</i>



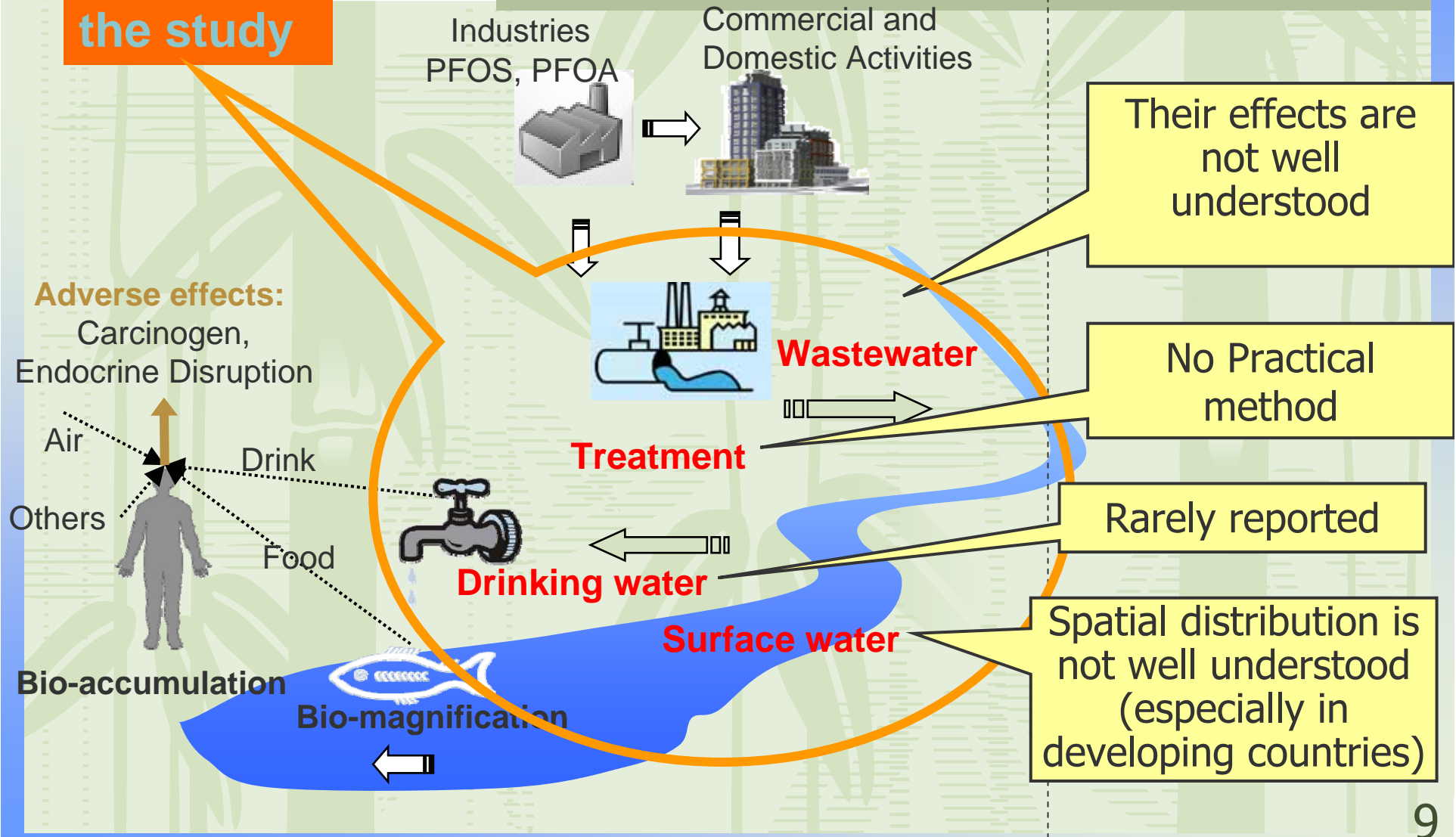
No of papers related PFOS/PFOA in a database (JDream II)



Range of Environmental Engineering

Scope of the study

Background

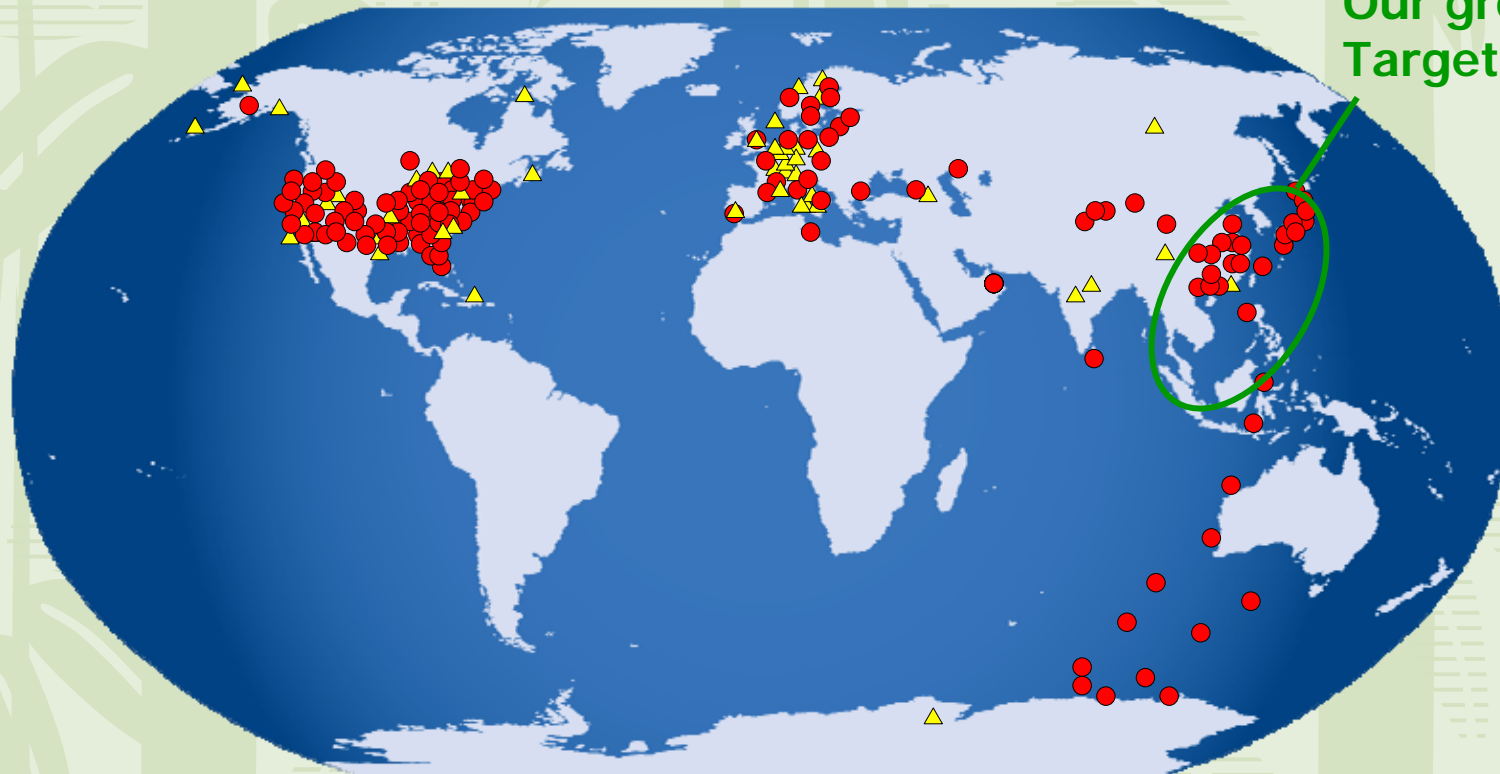




Surveys in the World

Introduction (POPs problem)
Perfluorinated compounds (PFCs)
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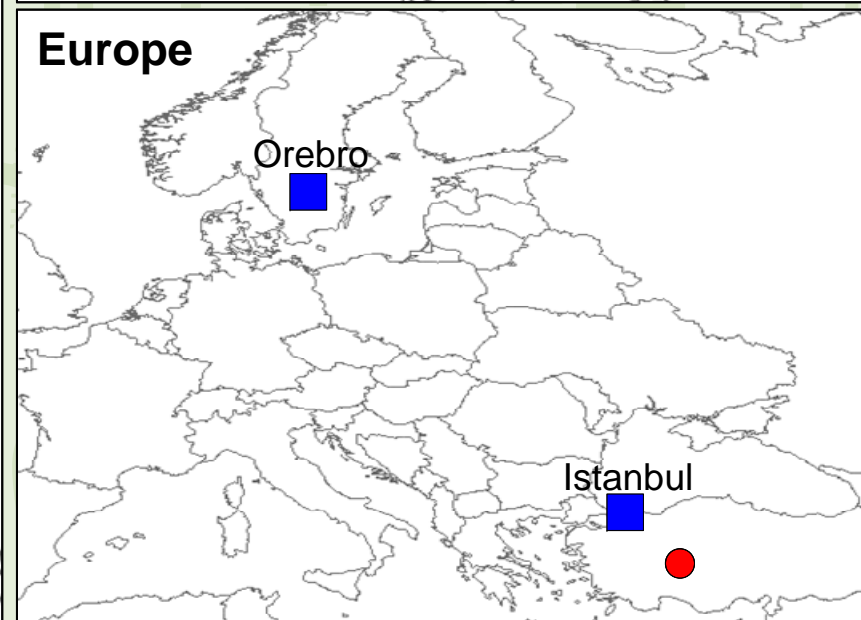
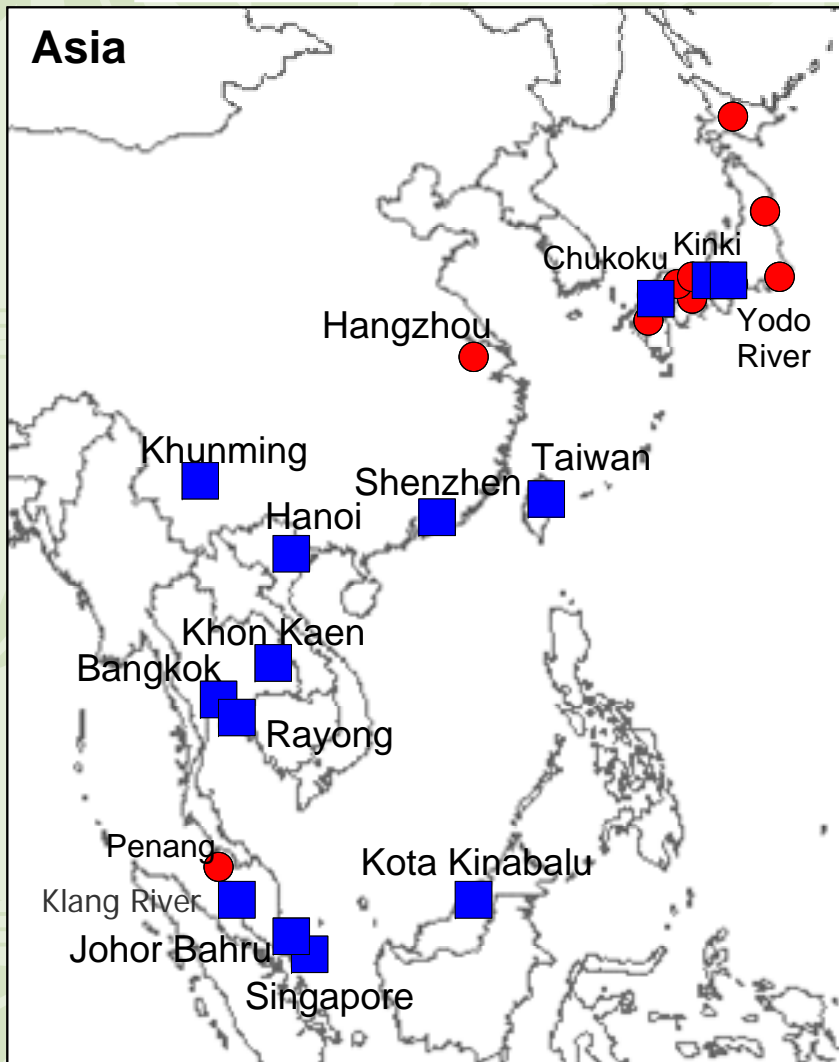
PFOS and PFOA are found in America, Europe and Japan, including *environment (water, air, food), human health, and wild animals.*



Our group
Target Area

PFCs (Red) in Water Environment and PFCs (yellow) in animals, 2007

2008/3/24



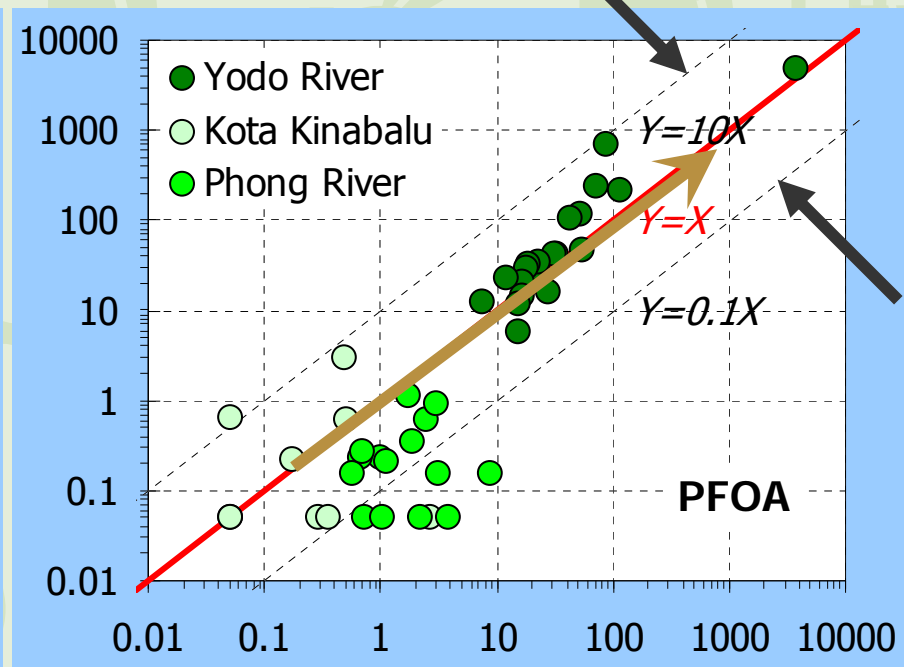
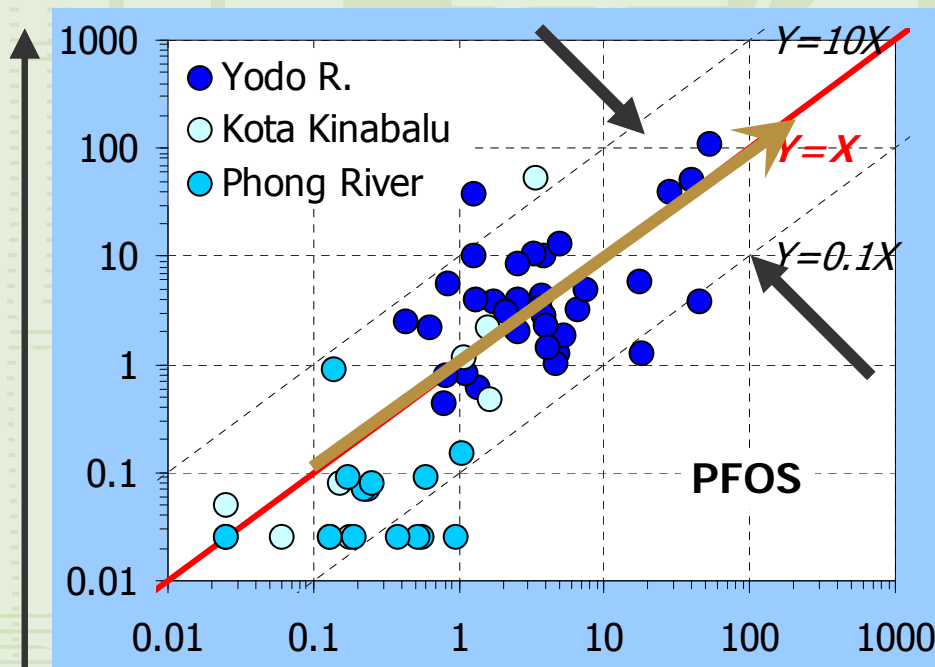
Sampling areas
(●:spot samples of tap water and surface water, ■:systematic survey)



I. Reproducibility of concentrations

Results of repeated sampling and analysis at different periods

Concentration (ng/L) in another sampling period

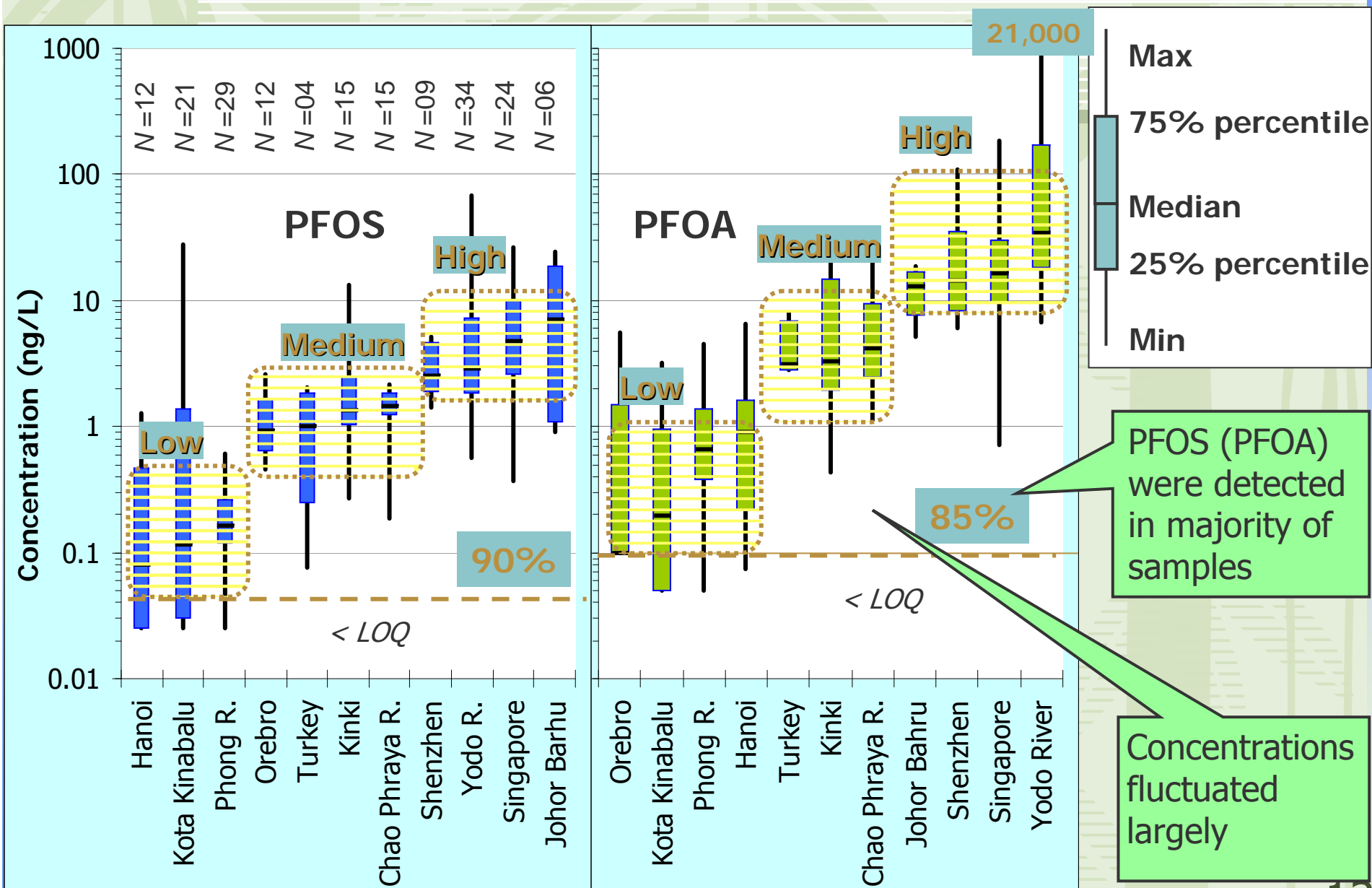


Concentration (ng/L) in a sampling period

Concentrations fluctuated within one order of magnitude
→ confirm concentration levels

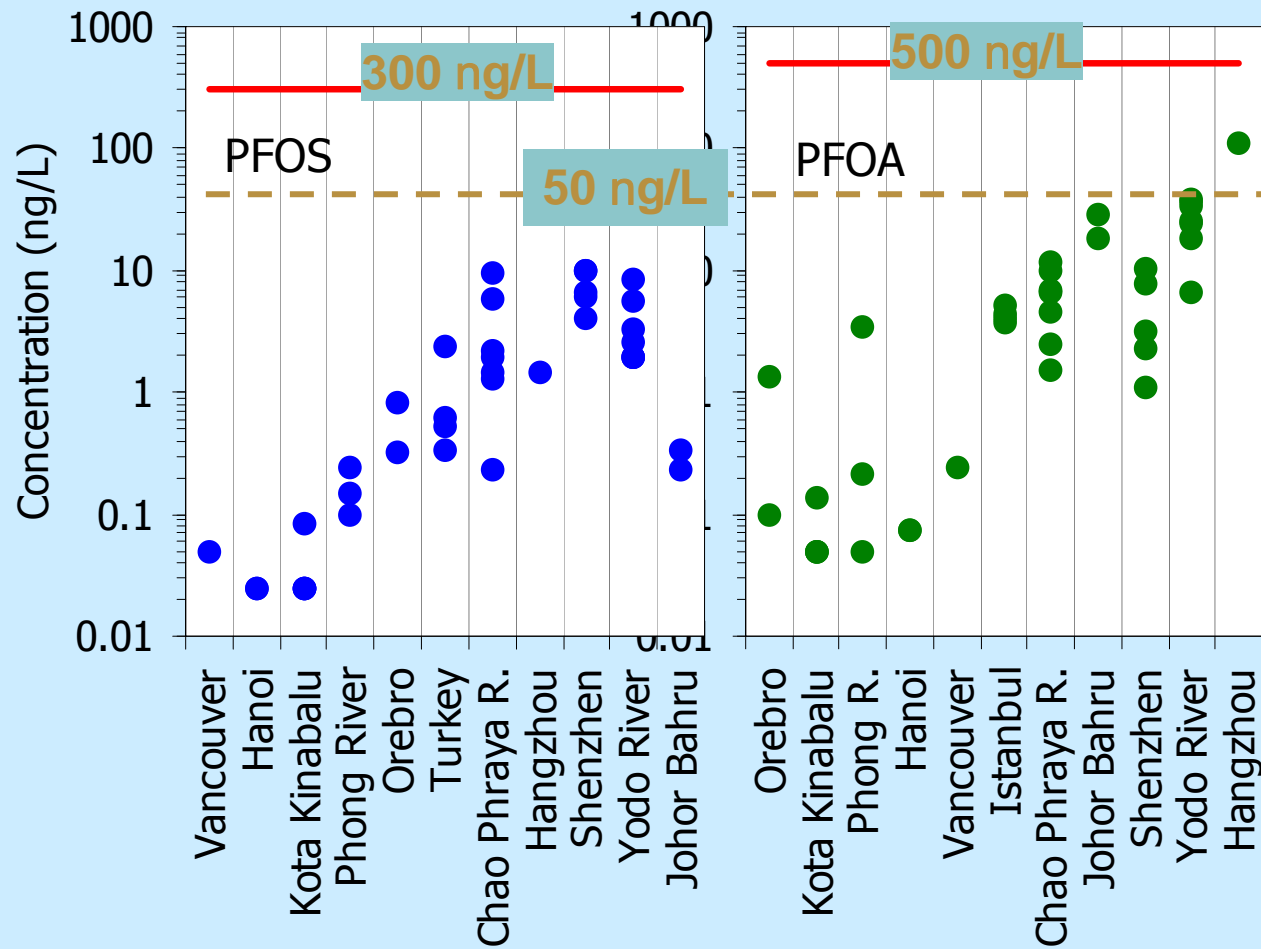


Concentrations in environmental waters





Tap water concentration



Safety levels recommended by Minnesota State (U.S.A.)

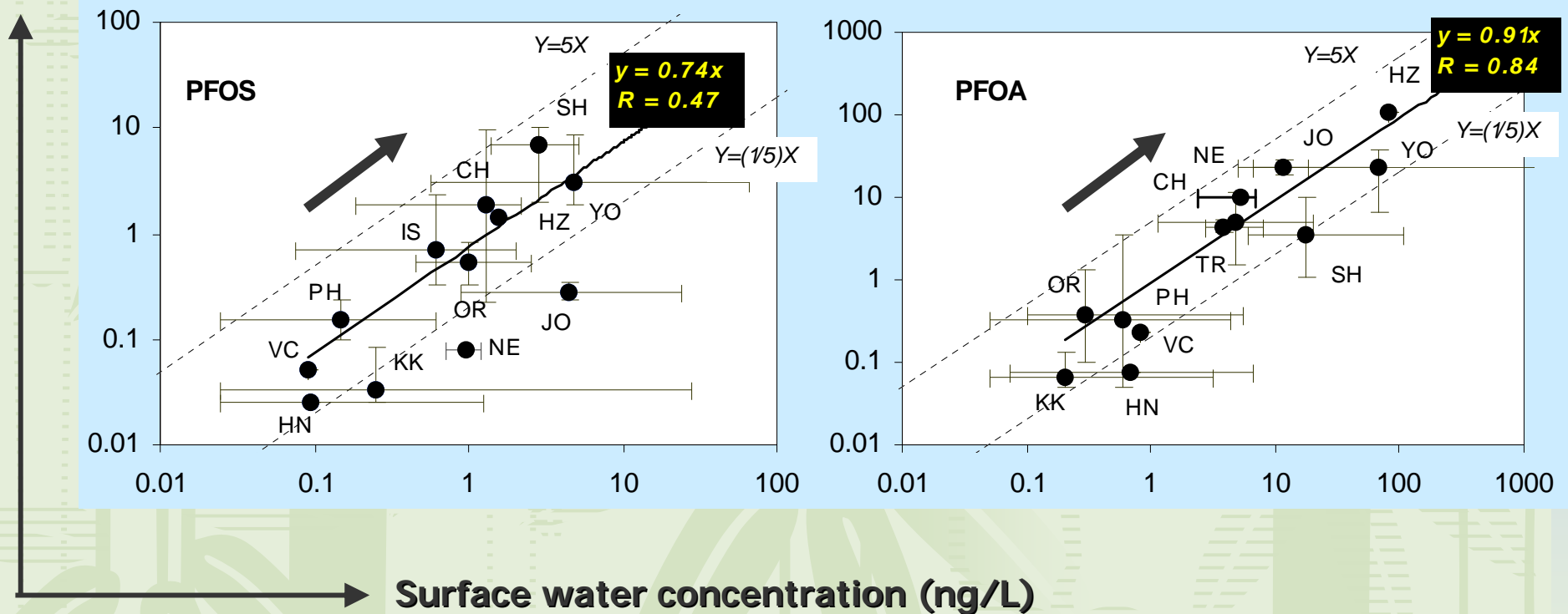
+25% increase in human blood concentrations (Harada *et al.* 2003)



Tap water vs surface water

YO : Yodo R.	OR : Orebro
CH : Bangkok	JO : Johor Bahru
SH : Shenzhen	IS : Istanbul
KK : Kota Kinablu	NE : Nevshehir
PH : Khon Kean	VC : Vancouver
HN : Hanoi	HZ : Hangzhou

Tap water concentration (ng/L)



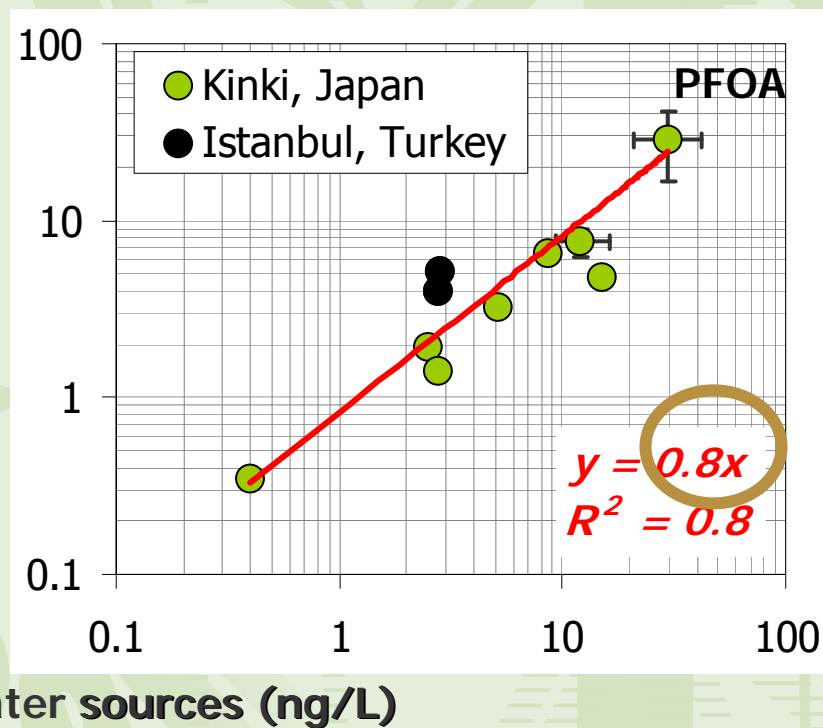
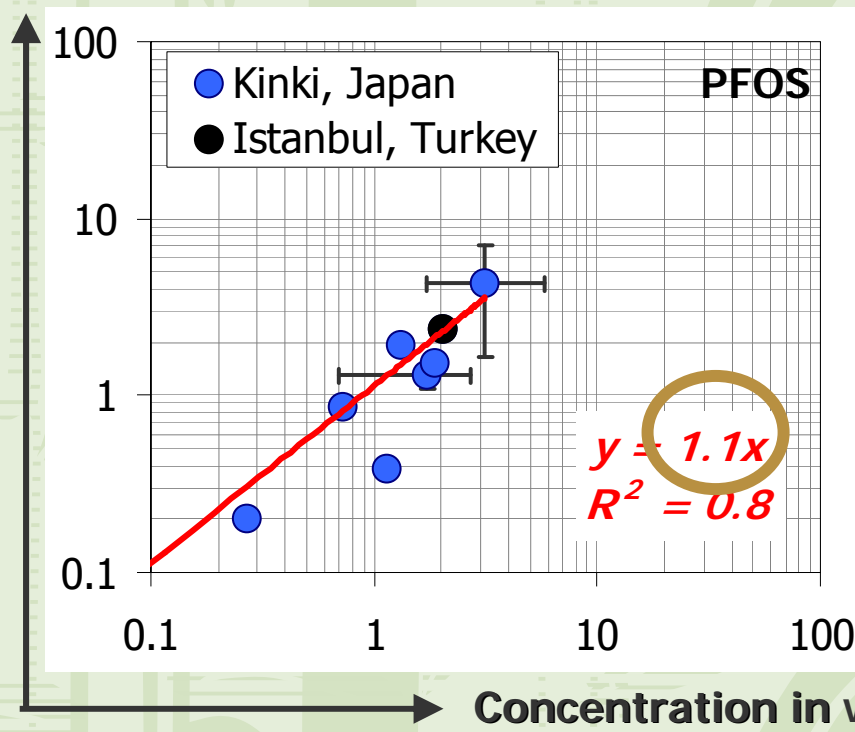
→ Concentrations in tap waters ~ in environmental waters: **SIMILAR!**

Water sources?



Water supply source - tap water

Concentration in tap water (ng/L)



Increasing trend of tap water concentrations versus water source concentrations
→ In general, PFOS and PFOA could not be effectively removed from water treatment steps.

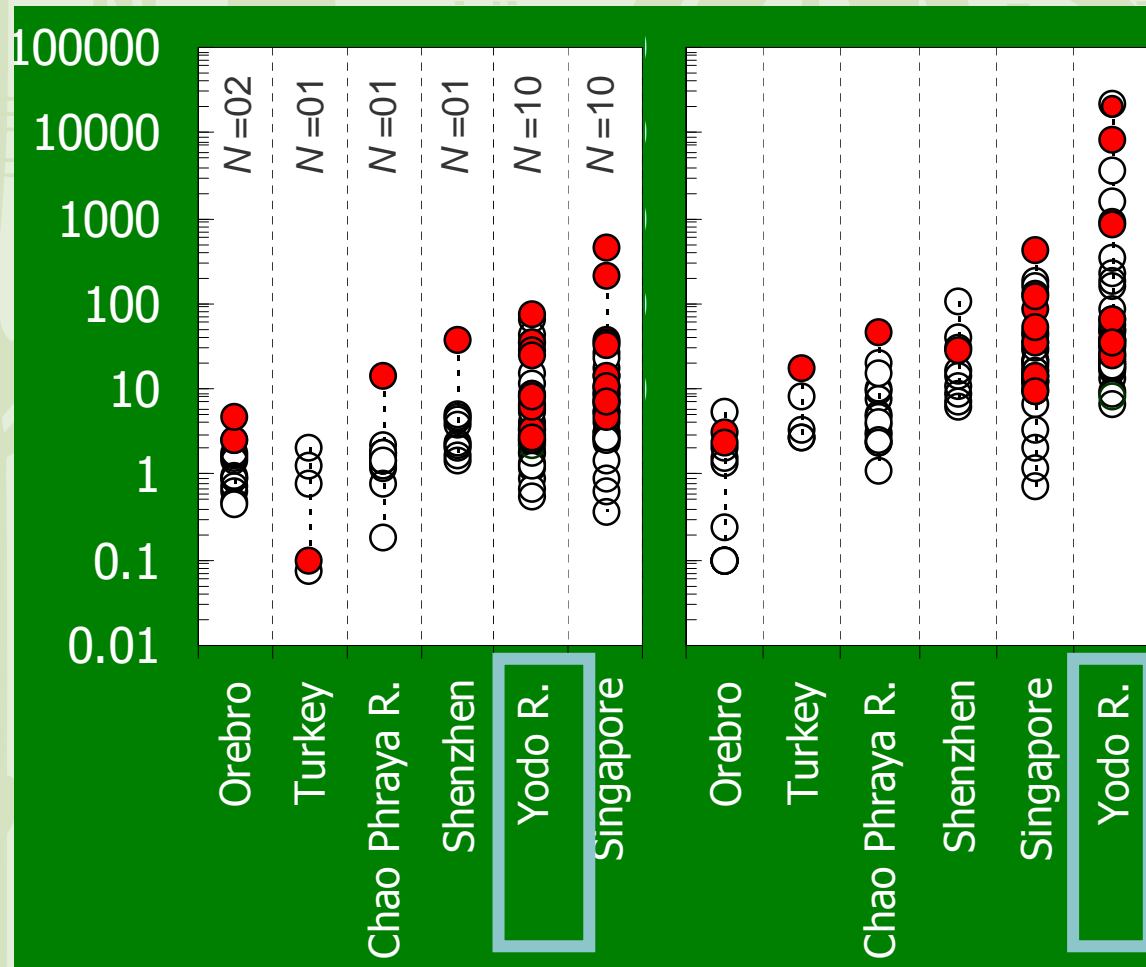


WWTP discharges

PFOS

PFOA

Concentration (ng/L)



WWTP discharges often had higher concentrations than environmental water did.

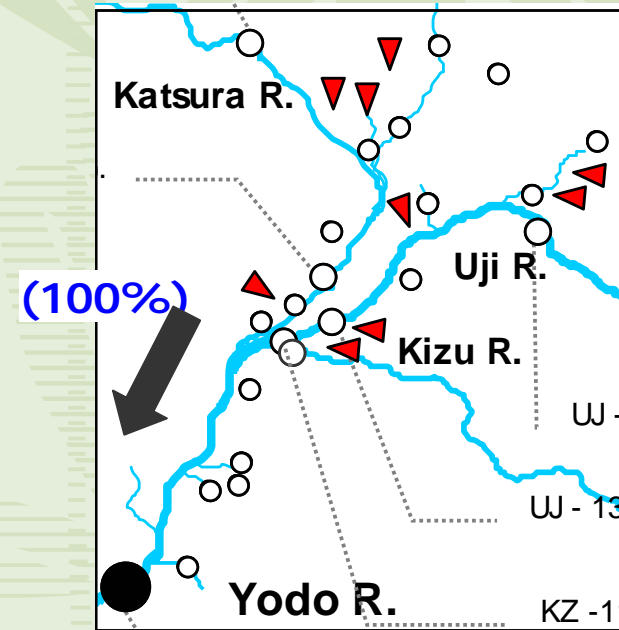
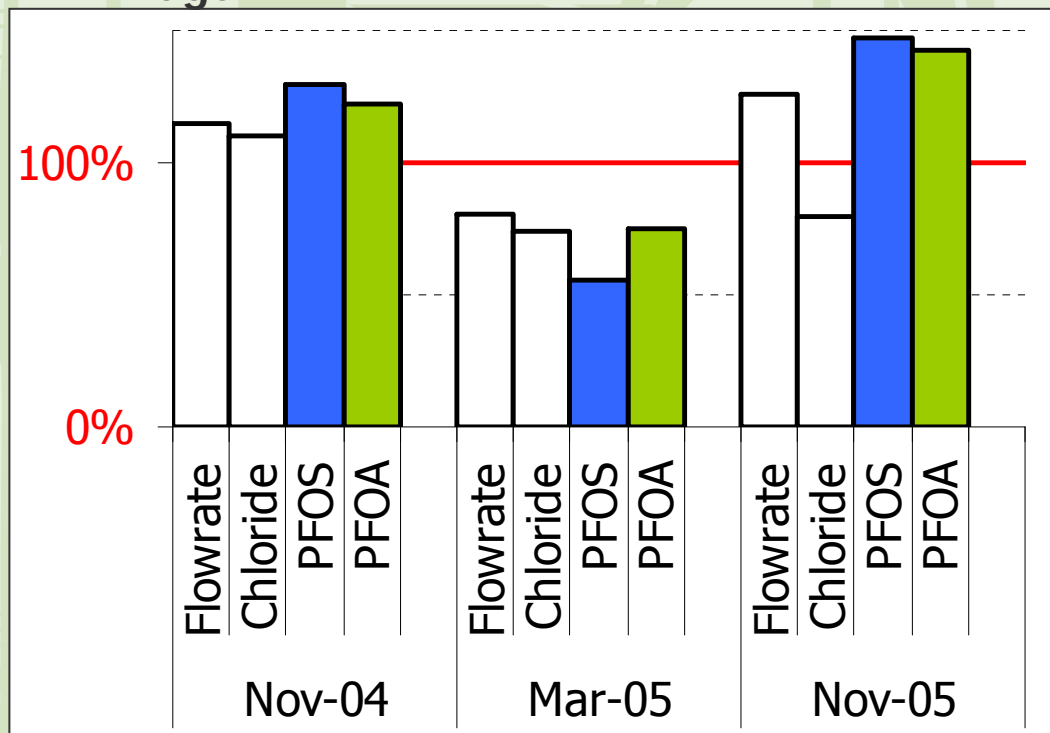
- WWTP discharges
- Surface water



Mass balance

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Mass flux contribution
 from upstream to Hirakata
 Bridge



Hirakata Bridge

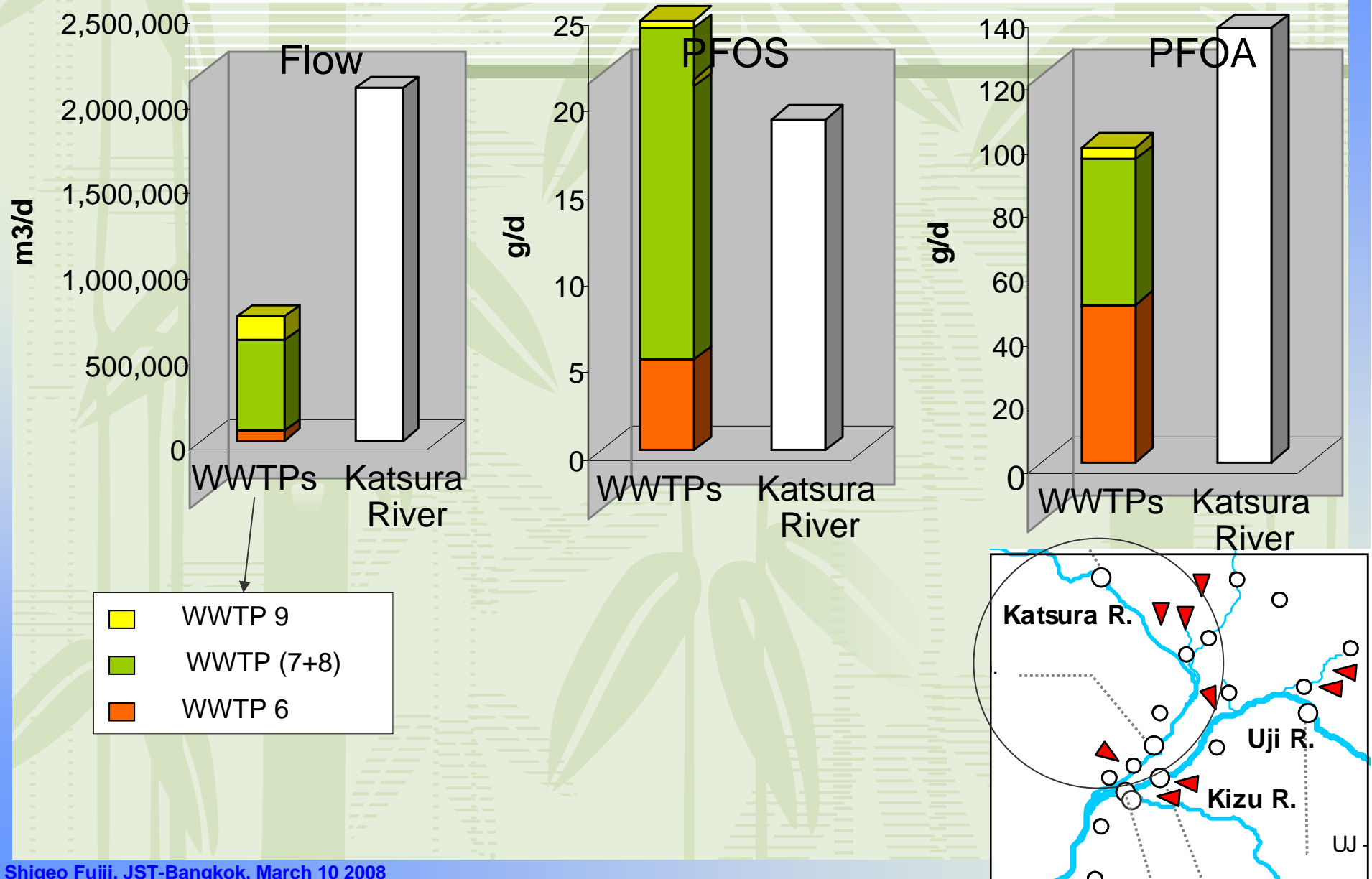


Good balance reflects no sink or rise of pollutants during transportation

(Reference: BOD is reduced to 1/3)



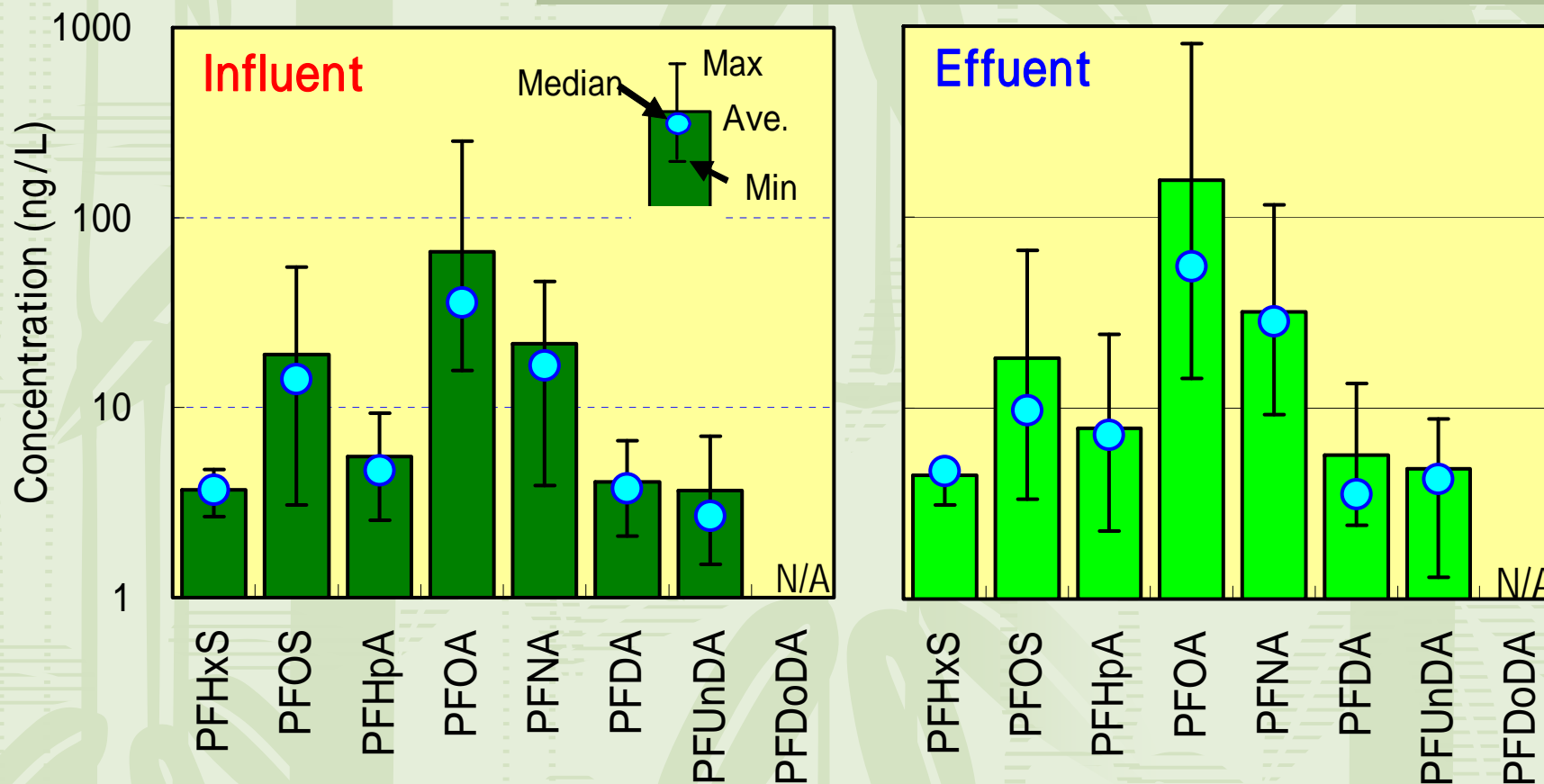
Contribution of WWTPs to Katsura River





Wastewater Treatment Plant Survey

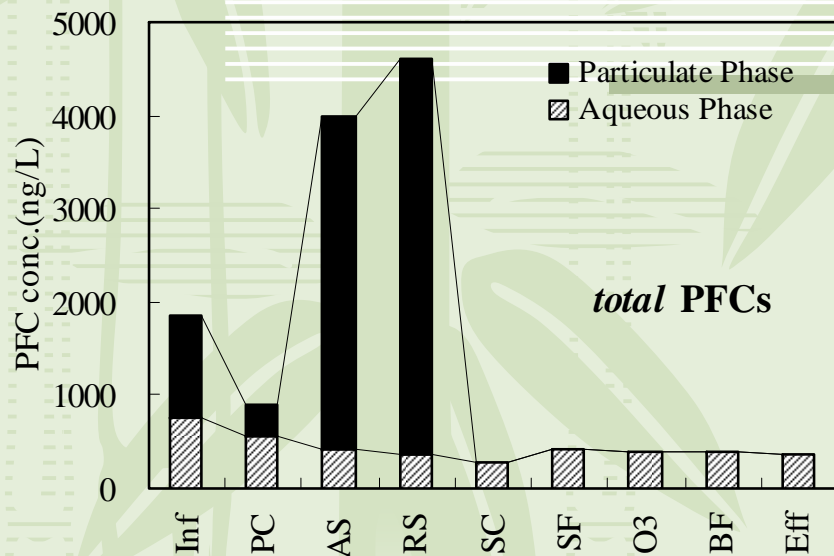
Japan (11), Singapore (4), China (1), Turkey (1)



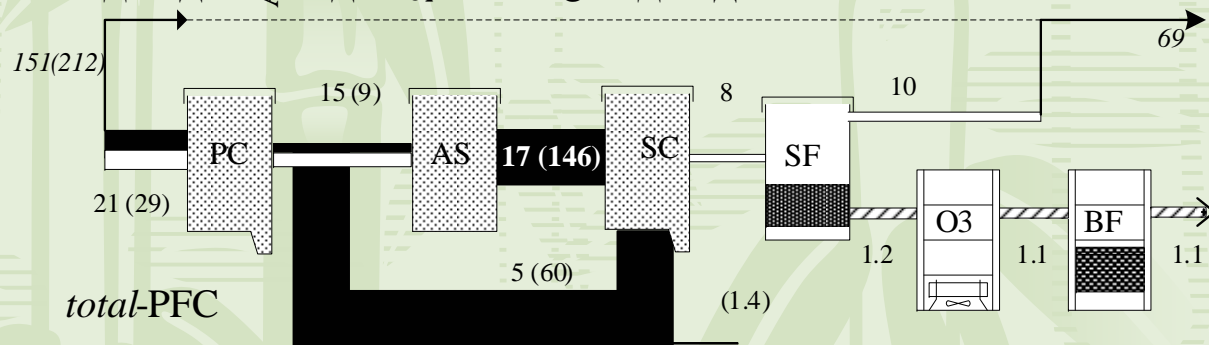
No obvious removal in WWTPs



Mass flux of total PFCs



1. 60% of total PFCs in influent was attached on particulate phase.
2. PFCs accumulated in activated sludge and circulated with return sludge
3. PFCs were not removed effectively. Ozone, BAC filter can not remove total PFCs.
4. 20% of total PFCs, or 50% of aqueous PFCs, were discharged to environment.



151(212) : aqueous (particulate) for WWTP

21 (29) : aqueous (particulate) for series 4

17 (146) : aqueous (particulate) in aeration tank

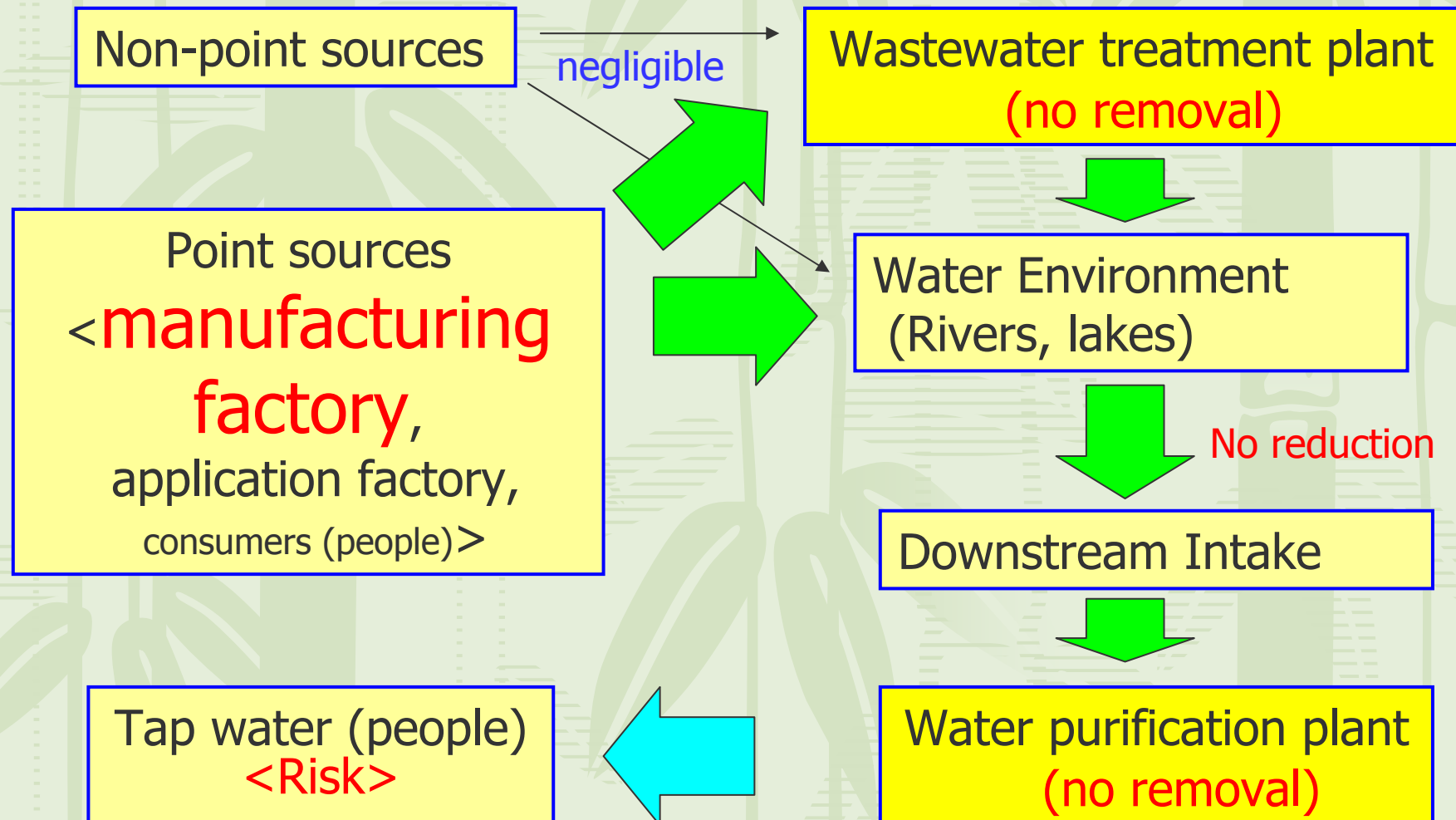
— : particulate phase, 10 g/day

— : aqueous phase, 10 g/day

▨ : aqueous phase, 1 g/day



Mechanism of Mass Flows and PFCs Risk





Possible Treatment

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When I started this research, PFOS was said to be tolerant to 1000°C Incineration, but....

- ❖ Biological Treatment
 - No decomposition is expected
- ❖ Physical treatment
 - ❖ Activated Carbon Adsorption: can remove to some extent
 - ❖ Membrane Filtration: Only RO is effective
- ❖ Chemical Treatment
 - ❖ UV Irradiation: effective for PFOA with long time
 - ❖ Ozonation: not effective
 - ❖ Super/ Sub critical water: effective
 - ❖ Chemical oxidation: Potassium persulfate is effective for PFOA

Still no practical method



Practical Measures

- ❖ In 2006, USEPA requested major PFOA manufacturing companies to phase out PFOA Product by 2015.
- ❖ In 2008, EU will exclude goods containing PFOS more than 0.005Wt% from markets.
- ❖ In 2008, COP4 of POPs convention will consider inclusion of PFOS in the list.

Still only PFOS and PFOA!!



Thank you/ありがとう/ขอบคุณครับ

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