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Emerging Contaminants in Drinking Water and Future Directions

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1. Introduction

The Japanese water quality standard and related items consist of three categories: water quality standard (51 items), management items (27 items including 102 agricultural chemicals), and items for further study (40 items). Among these chemicals, chlorate was introduced into the water quality standard in Apr. 2008 and the standard is lower than 0.6 mg/L. Chlorate was first thought to be a DBP in chlorine dioxide, but was found as a major DBP in sodium hypochlorite, which is a major disinfectant used in 85% of water treatment facilities.

2. Chemicals Included in Water Quality Standard and Related Items

Among the water quality standard and related items, chlorate is the most ubiquitous and the ratio of cases exceeding the 50% value of the standard was approximately half of the total water supply facilities in 2007. Chlorate is also found in bottled beverages. Among 106 bottled beverages purchased in Japan, chlorate was detected in 85 samples with a maximum level of 0.7 mg/L of chlorate.

Agricultural chemicals are managed using a holistic indicator, "total agricultural chemicals," which is the sum total of detected values divided by each target value, the so-called detected indicator (DI). In intensive monitoring, isoproturon, fenthion including its oxides, mefenacet, phenthoate, and cafenstrole are of relatively high importance in regard to the contribution to DI, especially in early summer, because they are mainly used in paddy areas as herbicides. However, DI does not necessarily exceed 1 in raw water and finished water.

3. Perchlorate in water sources

Perchlorate has been found at high concentrations in the upper Tone River and its tributary, Usui River, and the maximum concentrations were 340 and 2300 μg/L, respectively. The sources of perchlorate are the effluents from industrial perchlorate production and industry employing electrolysis processes for purposes other than its production. Due to the discharge of perchlorate into the upper Tone River Basin, perchlorate concentrations in the river water of the middle and lower Tone River Basin were generally 10–20 μg/L. The estimated population affected by this water is over 20 million. Thus, perchlorate has been newly included in the "items for further study" category and trials have been performed to encourage companies to control it before discharge. It is important to consider the effect of perchlorate, as it is known to inhibit iodine uptake. However, the Japanese diet generally includes more marine foods that diets from other regions.

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4. Occurrence of N-nitrosodimethylamine (NDMA)[2)]

A national survey of NDMA confirmed broad contamination of NDMA in water sources at the level of several ng/L, and relatively high concentrations of NDMA formed by ozonation, especially in the Yodo River Basin. To date, the maximum concentration detected in finished water is 10 ng/L in ozonated water.

In sewage treatment plants (STPs) located in the Yodo River Basin, NDMA concentrations before and after ozonation were 16–290 ng/L and 24–280 ng/L, respectively. At one STP in the area, an extremely high concentration of NDMA formation (10,000 ng/L) was found after ozonation in one influent water sample. NDMA precursors upon ozonation in the influent at the STP were identified as the anti-yellowing agents, 4,4'-hexamethylenebis(1,1-dimethylsemicarbazide) (HDMS) and 1,1,1',1'-tetramethyl-4,4'-(methylene-di-p-phenylene)disemicarbazide (TMDS).

5. PFOA, PFOS, PPCPs, and other chemicals

PFOA is of large concern in the Yodo River Basin, which includes a large PFC factory and PFOS is unevenly distributed in the Tokyo area. PPCPs are rather ubiquitous in the aqueous environment. Although PPCPs are highly prevalent due to population density,[3)] detection in drinking water is limited. Throughout the survey of 60 pharmaceuticals in 6 major water treatment plants in Japan, 2005–2007, fenofibrate (max. 31 ng/L), diclofenac (max.16 ng/L), and carbamazepine (max.25 ng/L) were the only pharmaceuticals detected in finished water. The maximum relative intakes, RI, calculated from the maximum concentration divided by the minimum daily dose for these agents were 1.6×10^{-7}, 3.2×10^{-7}, and 6.2×10^{-8}, respectively.

Priority setting for pharmaceutical monitoring is currently under investigation using various factors such as production, urinary excretion, solubility, biodegradation, reduction, and minimum daily dose. Haloperidol, tetracycline, hydralazine, ephedrine, dichlofenac, and valproic acid have been given higher priority.

In a national survey of chemicals in the water environment, bisphenol A, EDTA, p-octylphenol, p-dichlorobenzene, N,N-dimethylformamide, nonylphenol, and formaldehyde were detected at high prevalence.

6. Priority Setting for Chemical Management for Water Supply

With regard to controlling the increasing number of chemicals in the environment, strategic priority setting for chemical monitoring and management is attracting increasing attention. Considering the ratio of “Exposure/Standard (Reference Value),” area-specific and industrial chemicals such as perchlorate, NDMA, PFOA, PFOS, nitrate, nitrite, arsenic, and fluoride, which are relatively hydrophilic substances, are of higher priority. Priority must also be set for chemicals and DBPs in the water supply, including chlorate, trihalomethanes (THMs), haloacetic acids (HAAs), bromate, aluminum, and lead. Other chemicals that are physiologically active substances and toxic chemicals are also of interest, including agricultural chemicals, PPCPs, Bis A, POPs, dioxins, and PAHs, which are rather hydrophobic and can be reduced by water treatment.

References

1) Kosaka K., Asami M., Matsuoka Y., Kamoshita M. and Kunikane S., Occurrence of perchlrorate in drinking water sources of metropolitan area in Japan, ***Water Research*.** 41(15) 3474-3482, 2007

2) Identification of anti-yellow agents as N-nitrosodimethylamine precursors by ozonation from influent of a sewage treatment plant (submitted)

3) Nakada et al., Distribution of the PPCPs in 37 major Japanese rivers and population density of the catchments, ***Environ. Sci. Technol*.** 42(17) 6347-6353, 2008

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Japanese Water Quality Standard and Related Items

Water Quality Standard
(Water Works Law)

- Water works' responsibility for analysis
- Compulsory periodical investigation
- Heavy metals and chemicals detected above 10% of target values
- 31 Health related items + 20 Deteriorates

Management Items
(Director Notice, 2003)

- Director's request for analysis
- Subsidiary to the Water Quality Standard
- Items of provisional target values and low level detection
- Important items for water quality management
- 15 Health related items including total of 102 agricultural chemicals + 12 Deteriorates

Items for Further Study
(Advisory Council, 2003)

- Undefined toxicological evaluation
- No sufficient data in purified water
- 40 items listed for investigation

Subject to Rolling Revision

2

Japanese Water Quality Standard –Health Related Items

No	Item	(mg/l)	No	Item	(mg/l)
1	Standard Plate Count	100 colonies/ml	16	*cis*-1,2-Dichloroethylene	0.04
2	*E. Coli*	Not to be detected	17	Dichloromethane	0.02
3	Cadmium	0.01	18	Tetrachloroethylene	0.01
4	Chromium (IV)	0.05	19	Trichloroethylene	0.03
5	Mercury	0.0005	20	Benzene	0.01
6	Selenium	0.01	21	Chlorate	0.6
7	Lead	0.01	22	Bromate	0.01
8	Arsenic	0.01	23	Chloroform	0.06
9	Cyanide ion and Cyanogen Chloride	0.01	24	Dibromochloromethane	0.1
10	Nitrate and Nitrite	10	25	Bromodichloromethane	0.03
11	Fluoride	0.8	26	Bromoform	0.09
12	Boron	1	27	Total trihalomethanes	0.1
13	Carbon tetrachloride	0.002	28	Chloroacetic acid	0.02
14	1,4-dioxane	0.05	29	Dichloroacetic acid	0.04
15	1,1-dichloroethylene	0.02	30	Trichloroacetis acid	0.2
			31	Formaldehyde	0.08

Japanese Water Quality Standard -Deteriorates

No	Item	(mg/l)	No	Item	(mg/l)
32	Zinc	1	42	Nonionic surfactants	0.02
33	Aluminum	0.2	43	Phenols	0.005
34	Chloride Ion	200	44	2-Methylisobolneol	0.00001
35	Hardness (Ca,Mg)	300	45	Organic substances (TOC)	5
36	Iron	0.3	46	Taste	Not abnormal
37	Copper	1	47	Color	5 unit
38	Sodium	200	48	Odor	Not abnormal
39	Manganese	0.05	49	Total residue	500
40	Anionic surfactants	0.2	50	Turbidity	2 unit
41	Geosmin	0.00001	51	pH	5.8-8.6

Chlorate（ClO_3^-）

- First thought as a DBPs in chlorine dioxide, but found as a major DBP in hypochlorite.
- Chlorate is introduced to a new standard in Apr. 2008. The target value is 0.6mg/L.
  cf. WHO 0.7mg/L, CA 0.2mg/L
- Standard for Water Supply Chemicals is 0.5mg/L at the maximum dose expected, which would be lower to 0.4mg/L.

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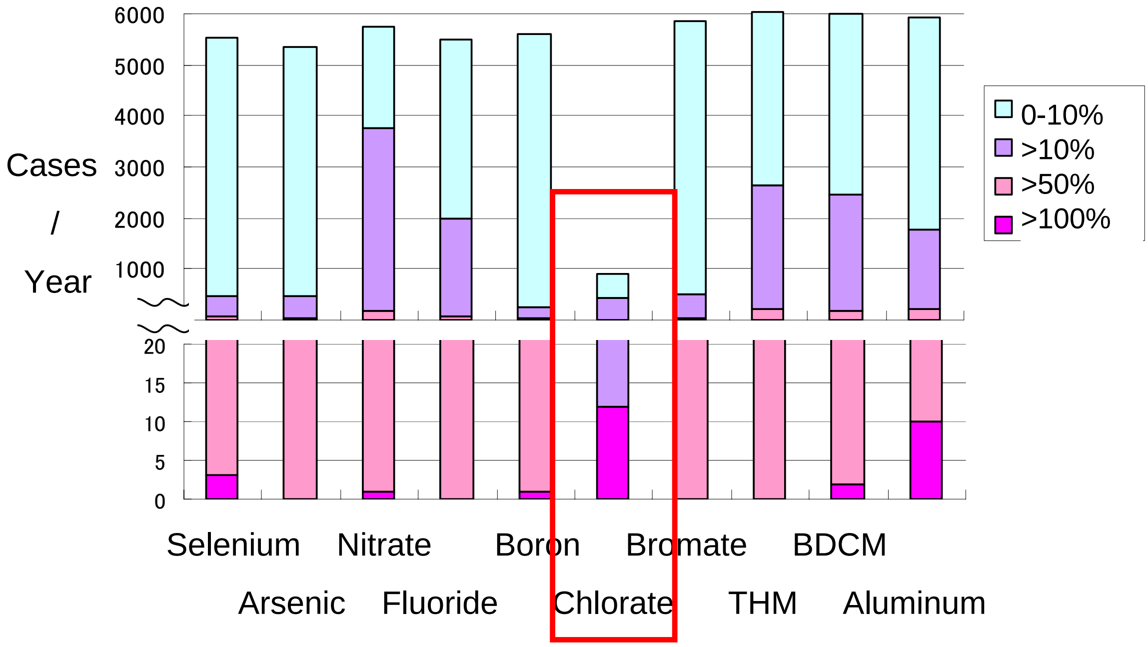
Items exceeding 10, 50 and 100% of the Standard value



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Chlorate in Bottled Water

	Detection	Max (μg/L)	Chlorate (μg/L) <10	<100	<600	600≦
Water supply	5/5	120	0	4	**1**	0
Natural*	34/49	100	46	2	**1**	0
Bottled	9/10	110	8	1	**1**	0
Tea	23/25	700	23	1	0	**1**
Soft drink	14/17	310	9	1	**7**	0

"Natural water" includes 3 supplied water containing ≥10 mg/L of chlorate, which should have labeled "water supply" water

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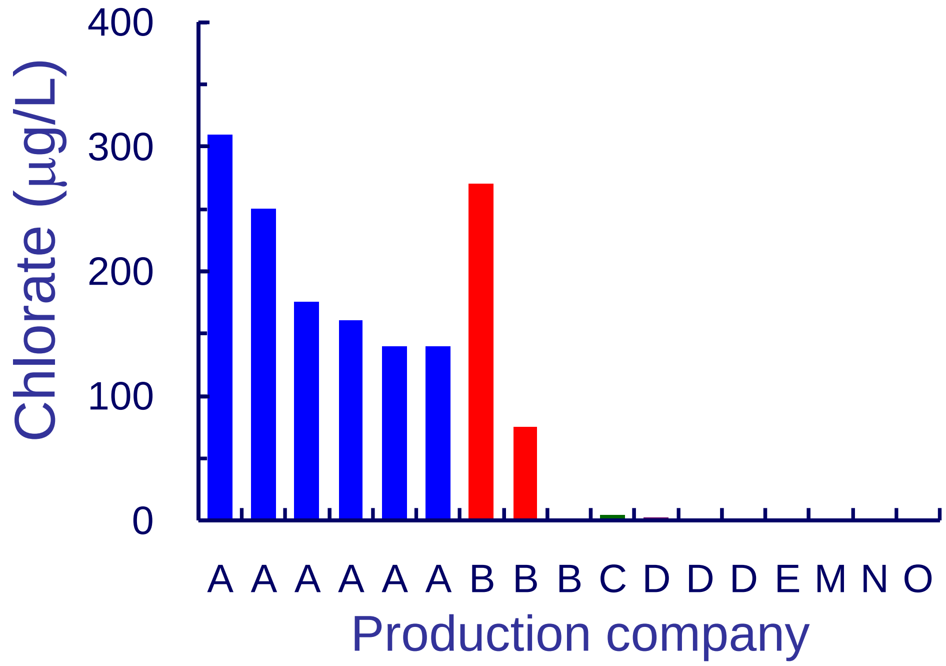
Chlorate in soft drinks according to their production company



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Management of Agricultural Chemicals

- Chemicals detected above 10% of target values
- None of agricultural chemicals categorized as water quality standard

- Available analytical methods
- Domestic shipping over 50 tons/year or detection history
- Management as
  "Total Agricultural Chemicals"
  -total sum of detected values divided by target values

$$DI = \sum_i \frac{DV_i}{GV_i} \le 1$$

- No available analytical methods for water
- Estimated domestic shipping over 50 tons/year

- Estimated domestic shipping below 50 tons/year

National Institute of Public Health **MHLW Advisory Council, 2003**

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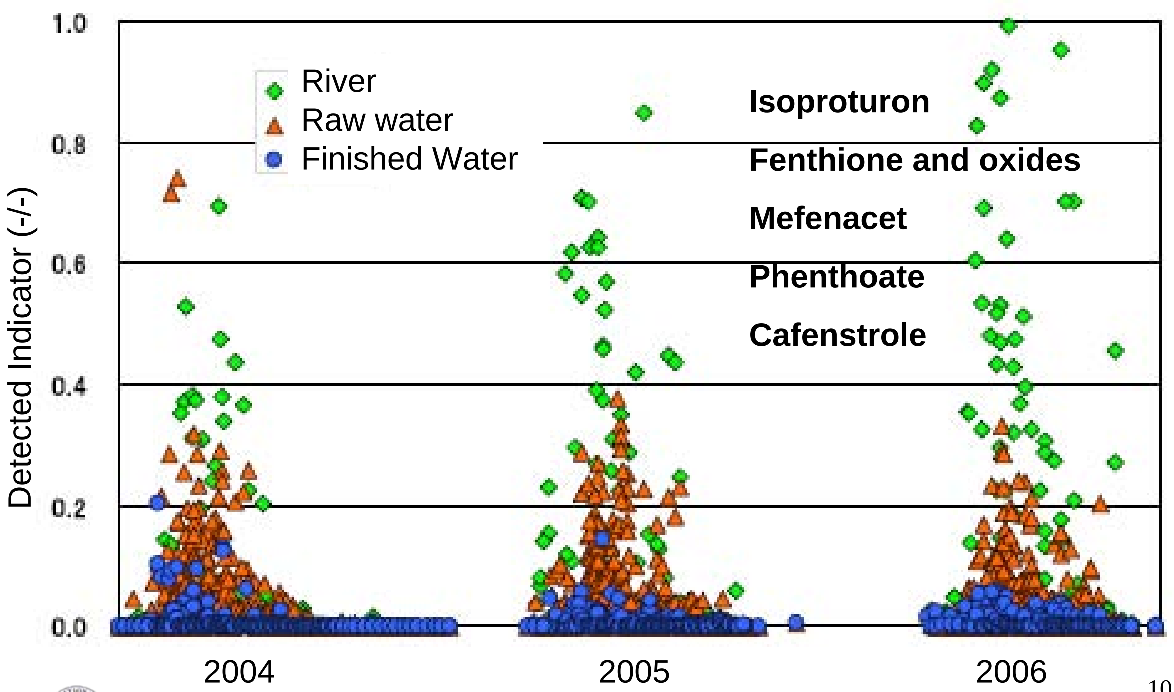
Agricultural chemicals (DI: total sum of detected values divided by each target value)



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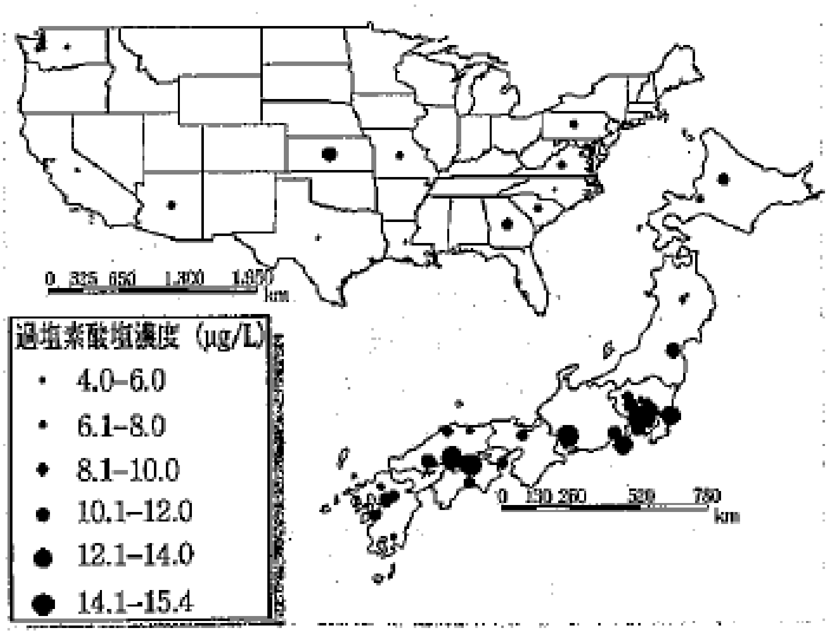
Perchlorate in dairy milk



Dyke, J. V., Ito, K., Obitsu, T., Hisamatsu, Y., Dasgupta, P. K., Blount, B. C.: Perchlorate in dairy milk. Comparison of Japan versus the United States, Environ. Sci. Technol., Vol.41, No.1, pp.88～92 (2007)

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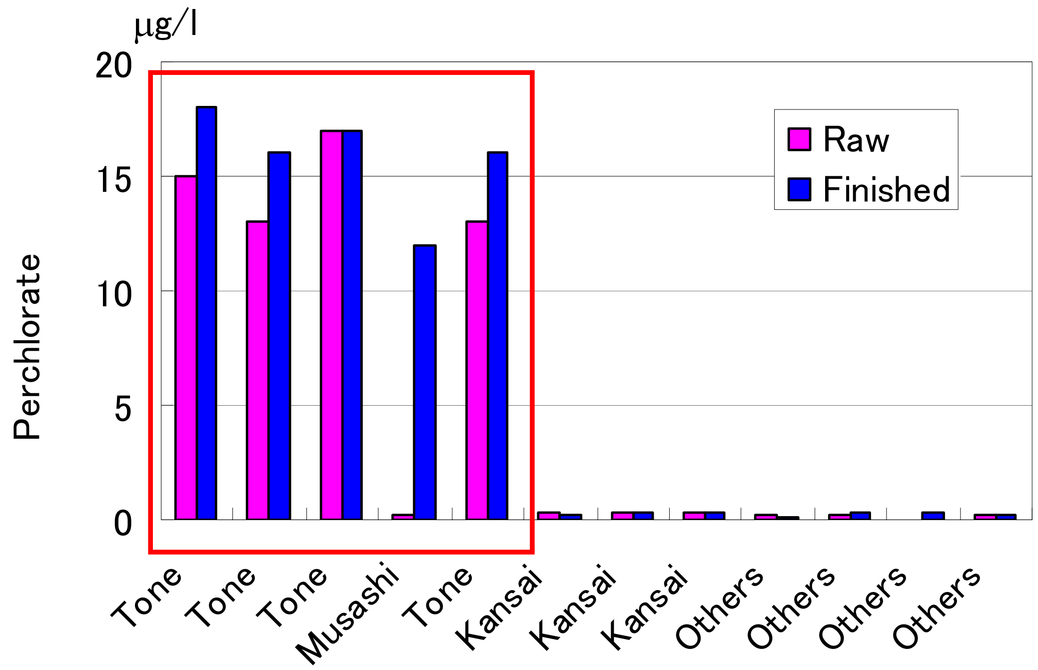
Perchlorate concentration in raw and finished water in Japan



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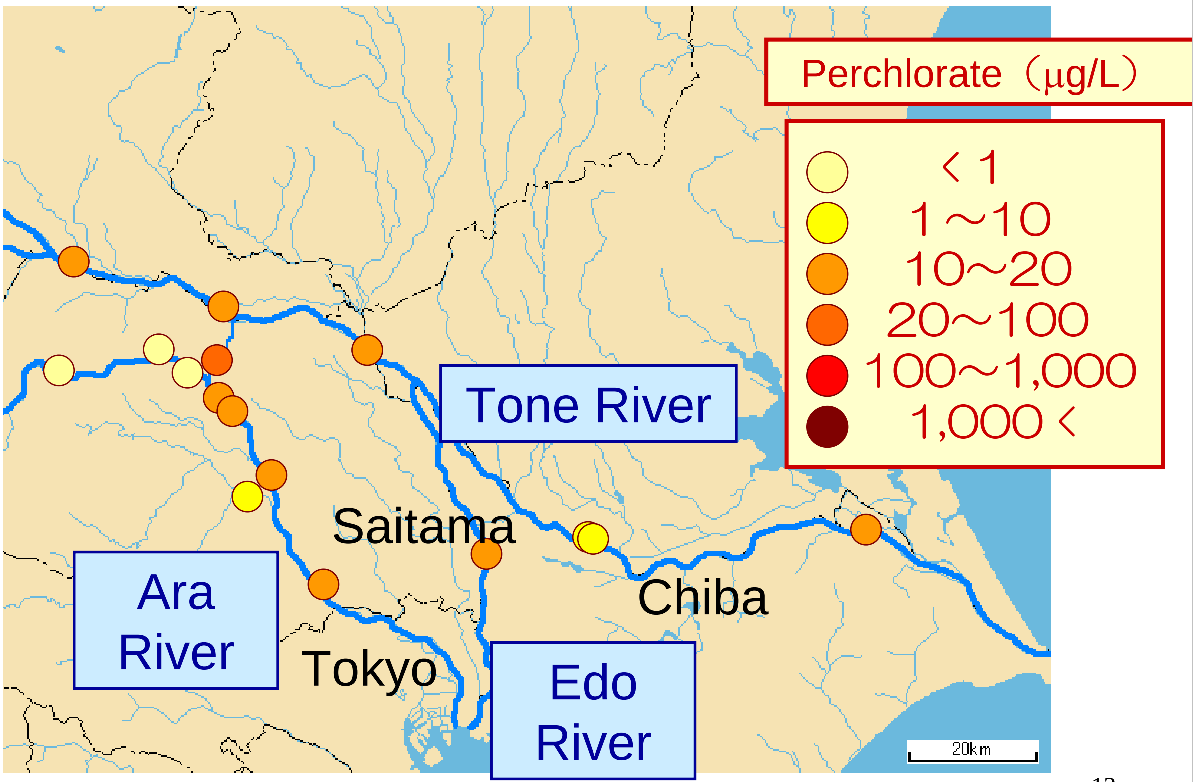
Perchlorate in the Tone River



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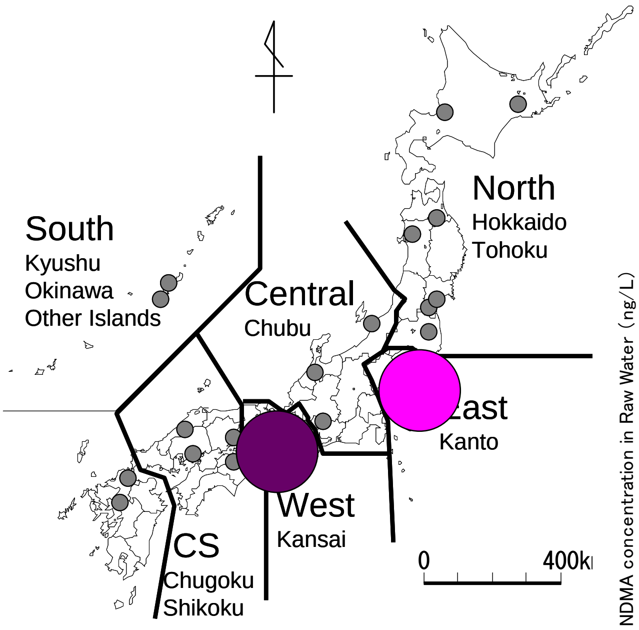
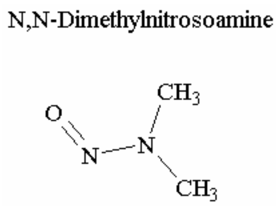
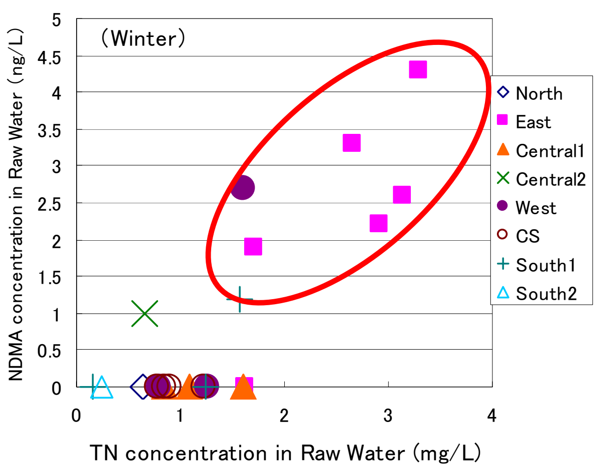
NDMA, dimethylnitrosoamine in Raw Water in Winter





NDMA
USEPA : 7ng/L
（10^{-5} cancer risk）
WHO GL : 100ng/L



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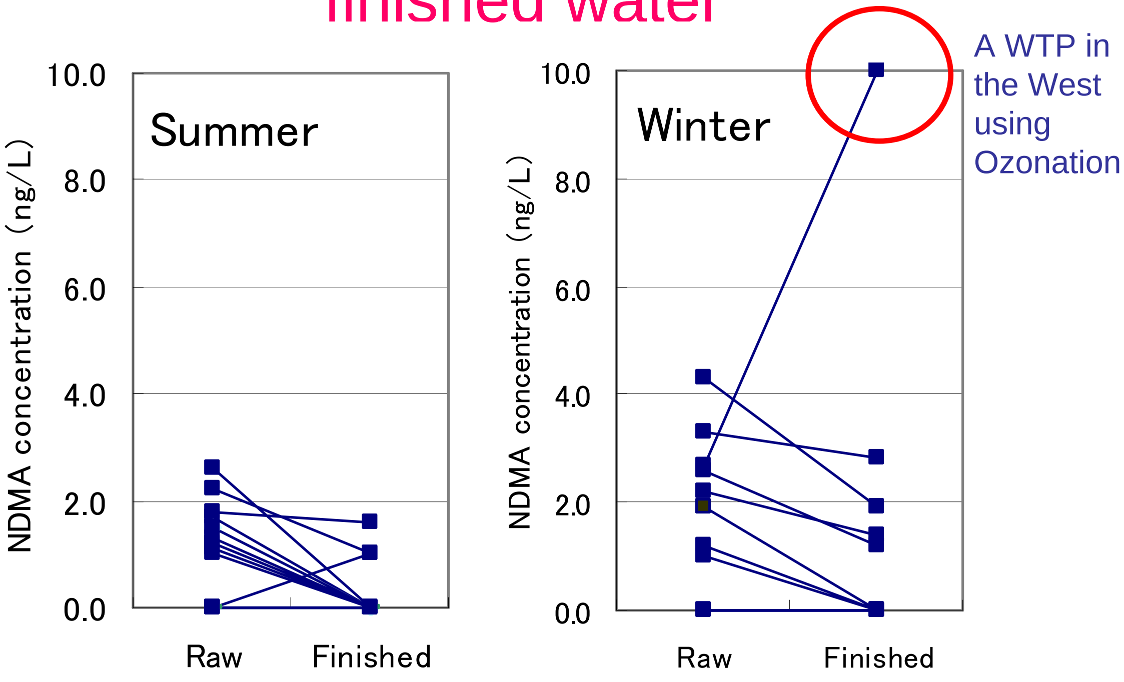
Detection of NDMA in raw and finished water



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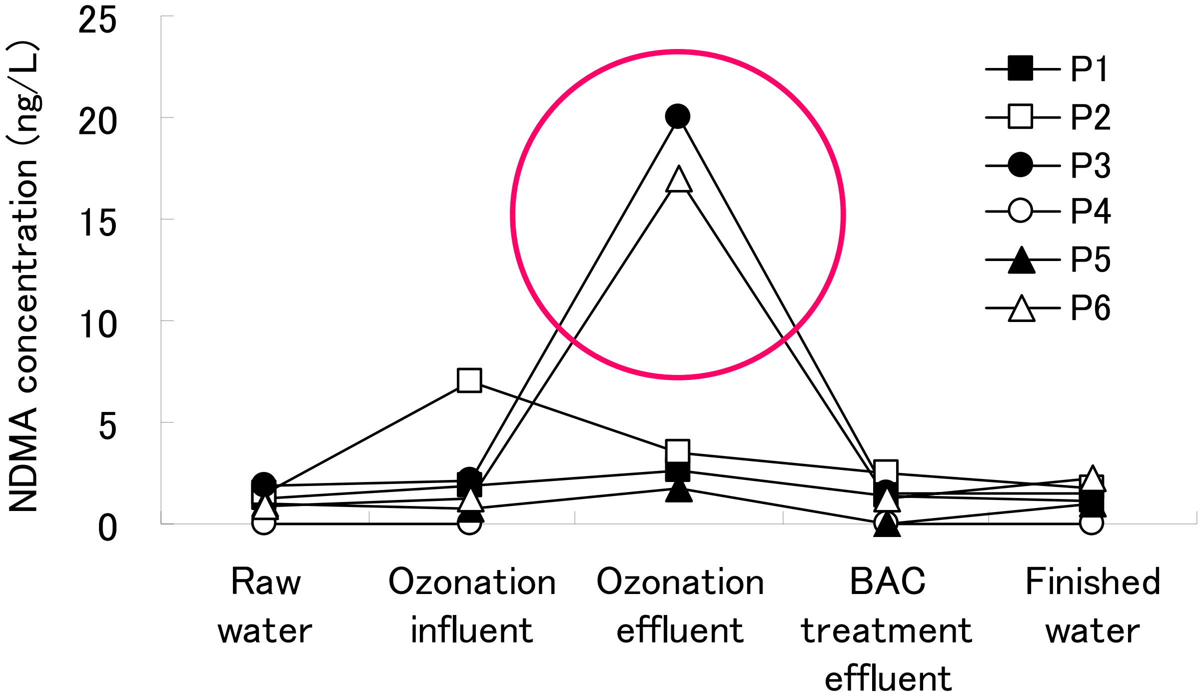
Fate of NDMA during ozonation in WTPs



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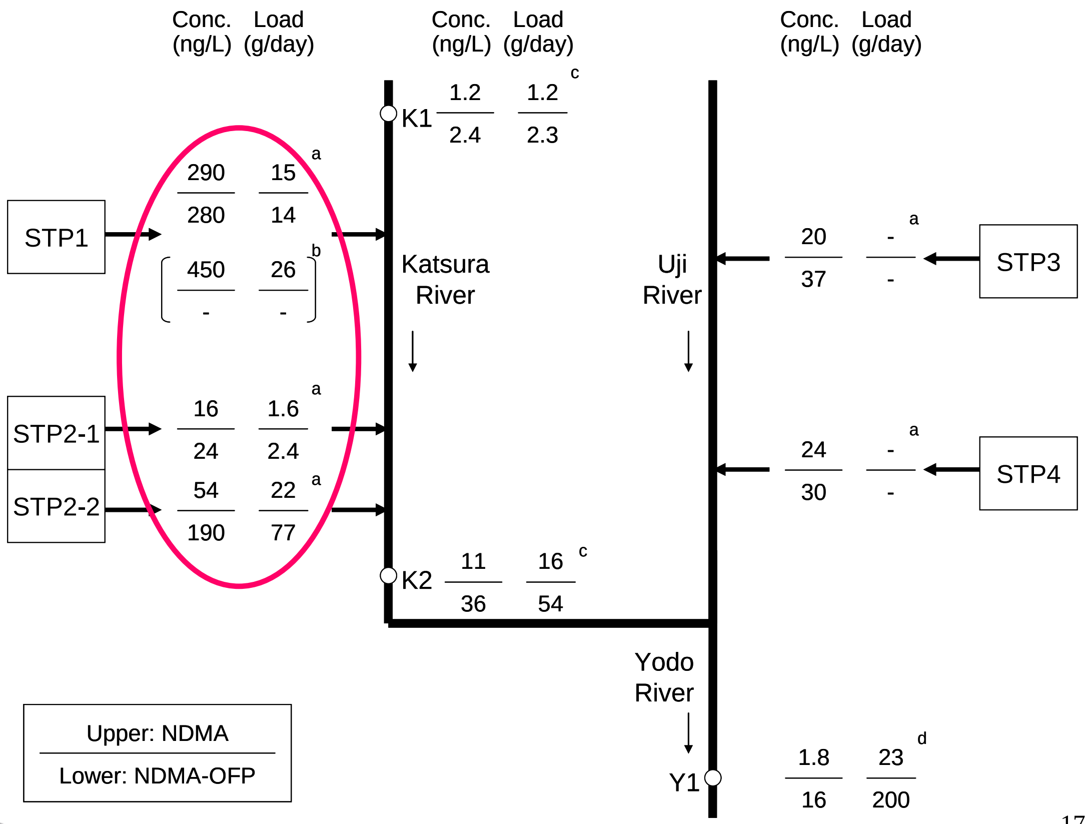
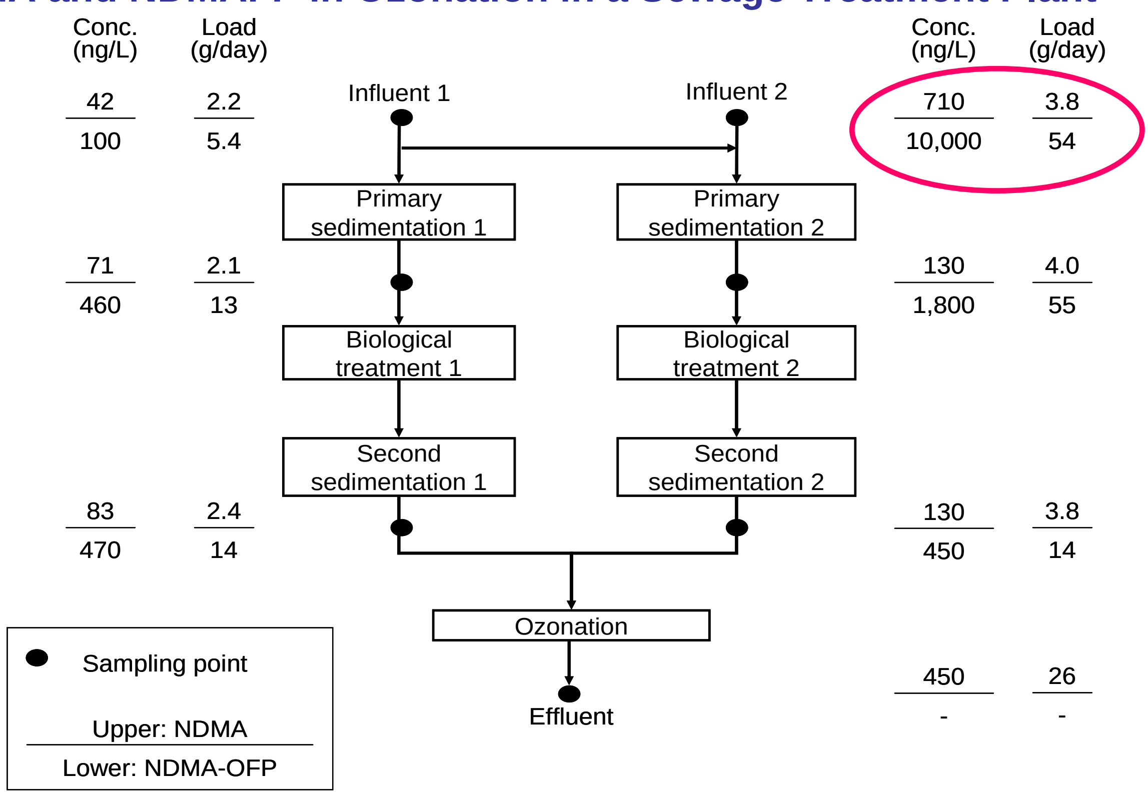
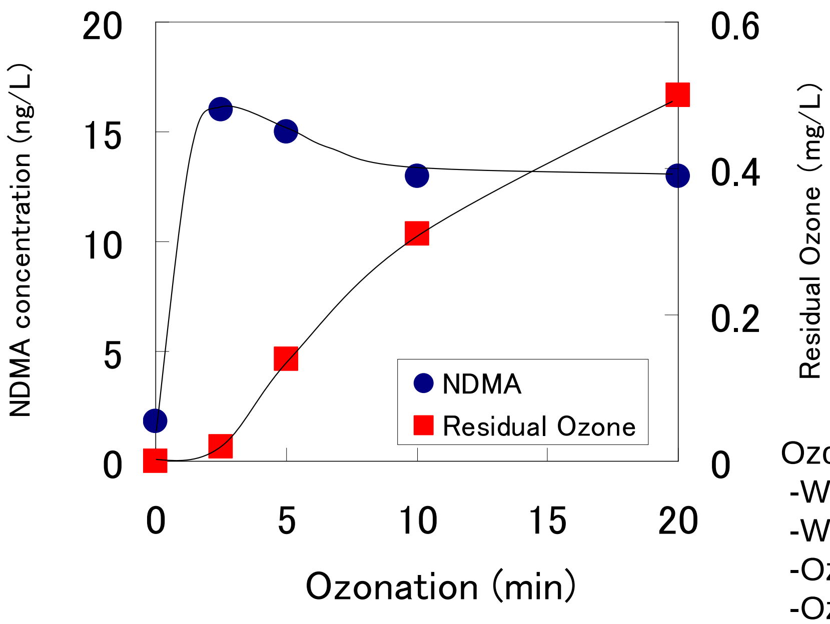
NDMA and NDMAFP in Ozonation in the Yodo River Basin in the West



NDMA and NDMAFP in Ozonation in a Sewage Treatment Plant



Formation of NDMA during ozonation of the Yodo River water



Ozonation Condition
- -Water Volume 1 litter
- -Water Temp. 20 ^{o}C
- -Ozone Gas 5mg/L
- -Ozone Gas Flow 0.5L/min

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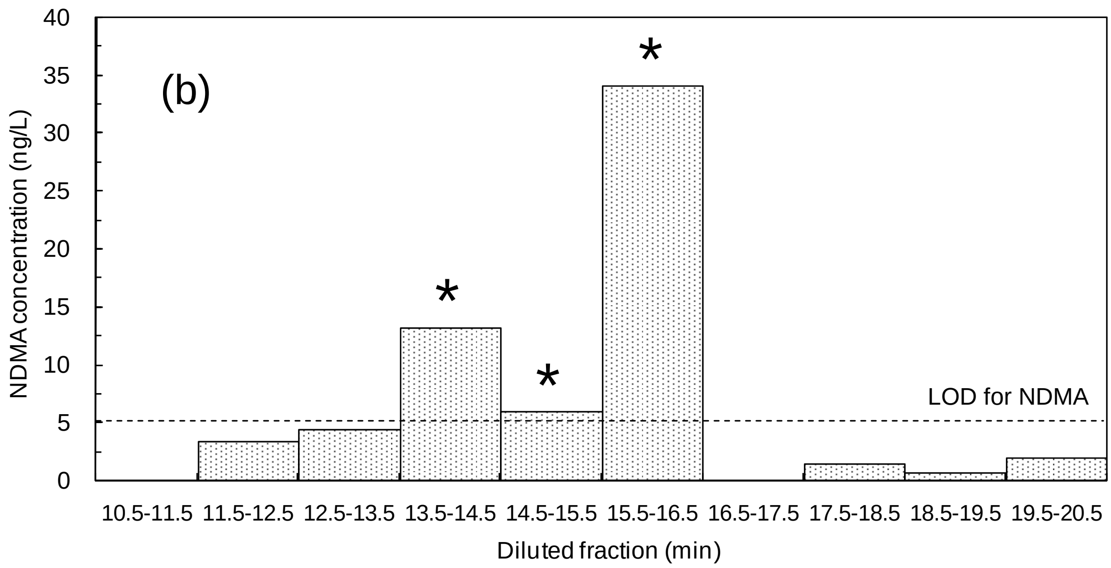
Identification of Anti-Yellow Agents as a precursor of NDMA in ozonation



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Chemicals found in aquatic environment,

6 chemicals detected among 33 chemicals in the Broadrange Survey

- 17β-estradiol
- Estron
- 2,4,6-Tribromophenol
- Polyoxyethylene alkylether
- Polyoxyethylene nonylphenylether
- 2-Methoxy-5-methyl aniline

8 chemicals detected among 13 chemicals in the Detailed Survey

- Bisphenol A
- EDTA
- p-Octylphenol
- p-Dichlorobenzene
- N,N-Dimethylformamide
- Nonylphenol
- PFOA
- PFOS

Ministry of Environment 2006 21

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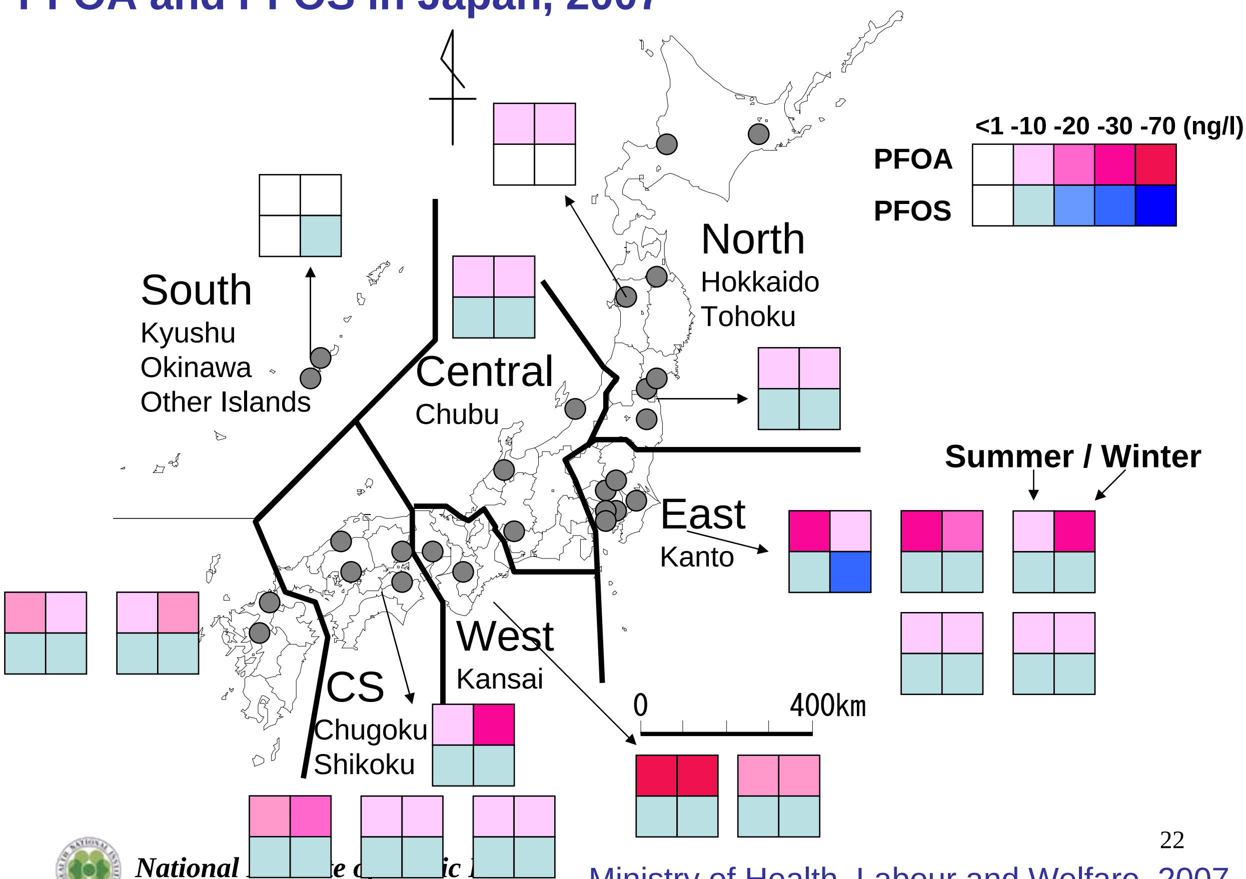
PFOA and PFOS in Japan, 2007



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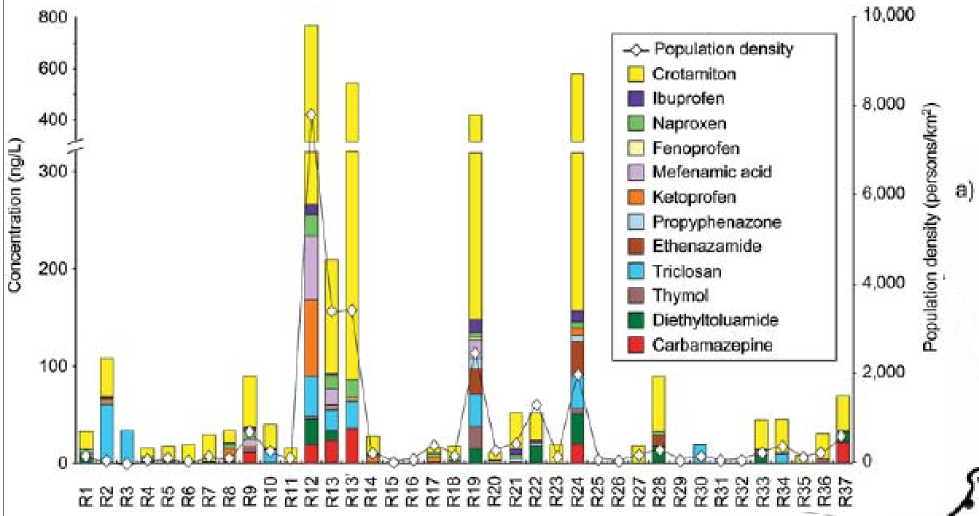
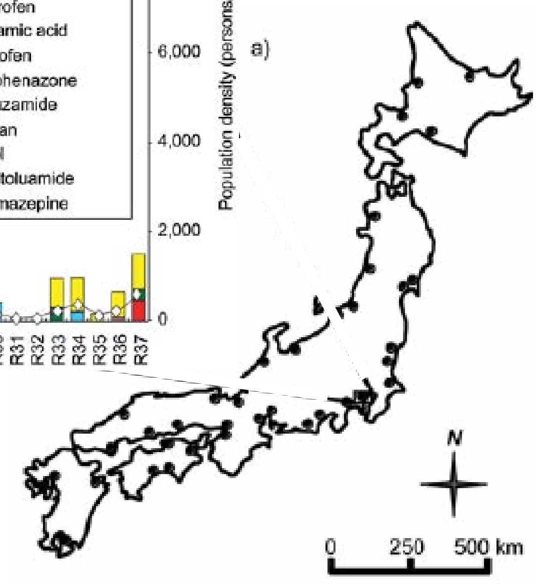
Ministry of Health, Labour and Welfare, 2007

Distribution of the PPCPs in 37 major Japanese rivers and population density of the catchments





Nakada et al., ***Environ. Sci. Technol.***, 42(17), 6347-6353, **2008**

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Examples of the pharmaceuticals detected at drinking water treatment plants in Japan

Pharmaceuticals	LoD (ng/L)	LoQ (ng/L)	Concentration in raw water at drinking water treatment plants (ng/L)						
			A	B	C	D	E	F	G
Aspirin	2	6	**7**	**8**	4	**8**	2	5	N.D.
Ibuprofen	0.4	2	1.7	**2**	N.D.	N.D.	0.7	**2.8**	N.D.
Acetaminophen	4	20	8	N.D.	7	N.D.	N.D.	N.D.	N.D.
Ketoprofen	0.8	3	N.D.	N.D.	**5.7**	N.D.	N.D.	N.D.	N.D.
Indometacin	0.4	2	**4.9**	**4.4**	**33**	0.9	1.1	**8.3**	N.D.
Iopamidol	8	30	**32**	9	25	N.D.	N.D.	15	N.D.
Iopromide	8	30	N.D.	9	12	N.D.	N.D.	14	N.D.
Sulfisozole Sodium	1	3	N.D.	N.D.	N.D.	N.D.	**4**	**7**	N.D.
Sulfamethoxazole	0.6	2	**3**	**3.4**	**10**	0.8	N.D.	**5**	**9**
Sulfadimethoxine	2	6	N.D.	N.D.	**45**	N.D.	N.D.	N.D.	N.D.

- 27 out of 60 pharmaceuticals were detected from raw water.
- Most of the pharmaceuticals were removed by advanced drinking water treatments.

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Pharmaceuticals detected* in finished water (2005-2007)

	Detection Limit (ng/L)	Max Conc C (ng/L)	Minimum Daily Dose D (mg)	Max Relative Intake** (C/D)
Fenofibrate	0.2	31	100	1.6×10^{-7}
Diclofenac	2.5	16	25	3.2×10^{-7}
Carbamazepine	0.2	25	200	6.2×10^{-8}

*These are only pharmaceuticals detected out of 60 pharmaceuticals investigated in finished water of 6 WTPs during 2005-2007. **Max relative intake was calculated using the maximum concentration among the data obtained 2005-2007, that was divided by the Minimum Daily Dose in the literature, assuming 2 litter of daily water consumption.

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Priority setting for pharmaceuticals

=detected in environment	Production	Urinary excretion	Solubility	Biodegradation	Reduction	Sum (S)	Minimum Daily Dose (D)	Ratio (S/D)
Haloperidol	1	1	2	4		8	1	8.0
Tetracycline	1	1	5	4	1	12	2	6.0
Hydralazine	2	4	5	3		14	3	4.7
Ephedrine	1	5	5	3		14	3	4.7
Dichlofenac	2	1	4	4	1	12	3	4.0
Valproic acid	4	4	5	3		16	4	4.0
Caffeine	3	1	4	3	5	16	4	4.0
Pantethine	3		5	4		12	3	4.0

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=detected in environment (yellow)	Production	Urinary excretion	Solubility	Biodegradation	Reduction	Sum (S)	Minimum Daily Dose (D)	Ratio (S/D)
Furosemide	1	5	3	3		12	3	4.0
Chlorpheniramine Maleate			5	3		8	2	4.0
Acetaminophen	4	1	4	3	3	15	4	3.8
Ketoprofen	3	1	3	3	5	15	4	3.8
Sulpiride	3	5	4	3		15	4	3.8
Sulpyrine	3	4	5	3		15	4	3.8
Sotalol		4	4	3		11	3	3.7
Bezafibrate		4	2	3	5	14	4	3.5
Levofloxacin		5	5	4		14	4	3.5

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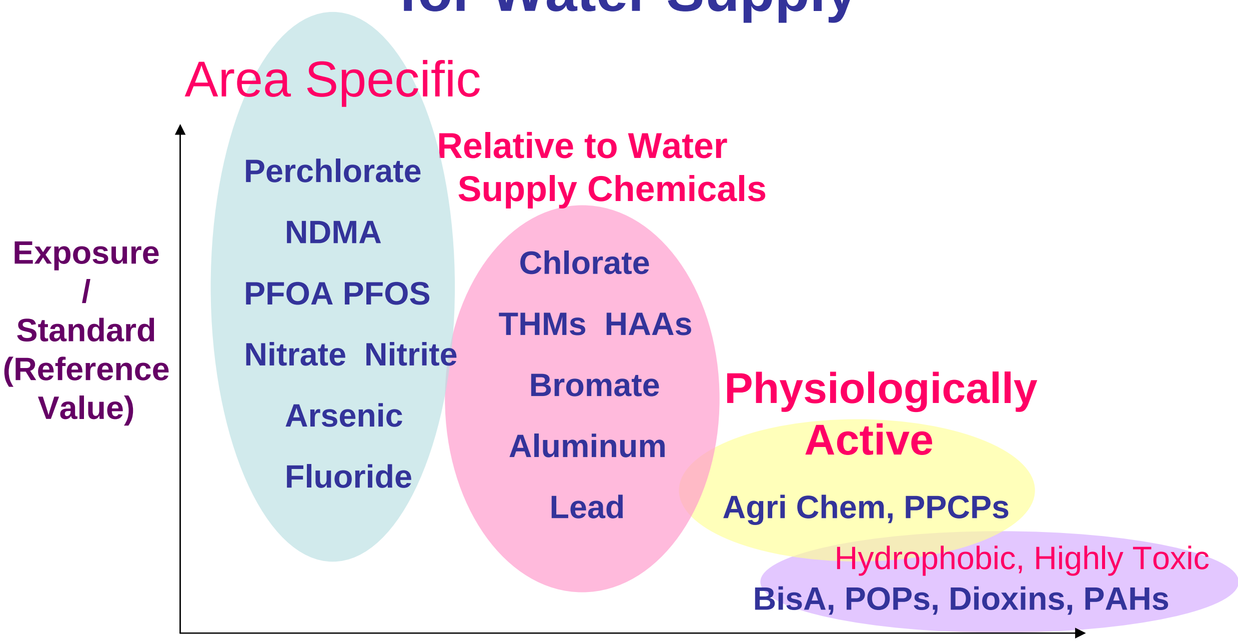
Priority Setting for Chemical Management for Water Supply



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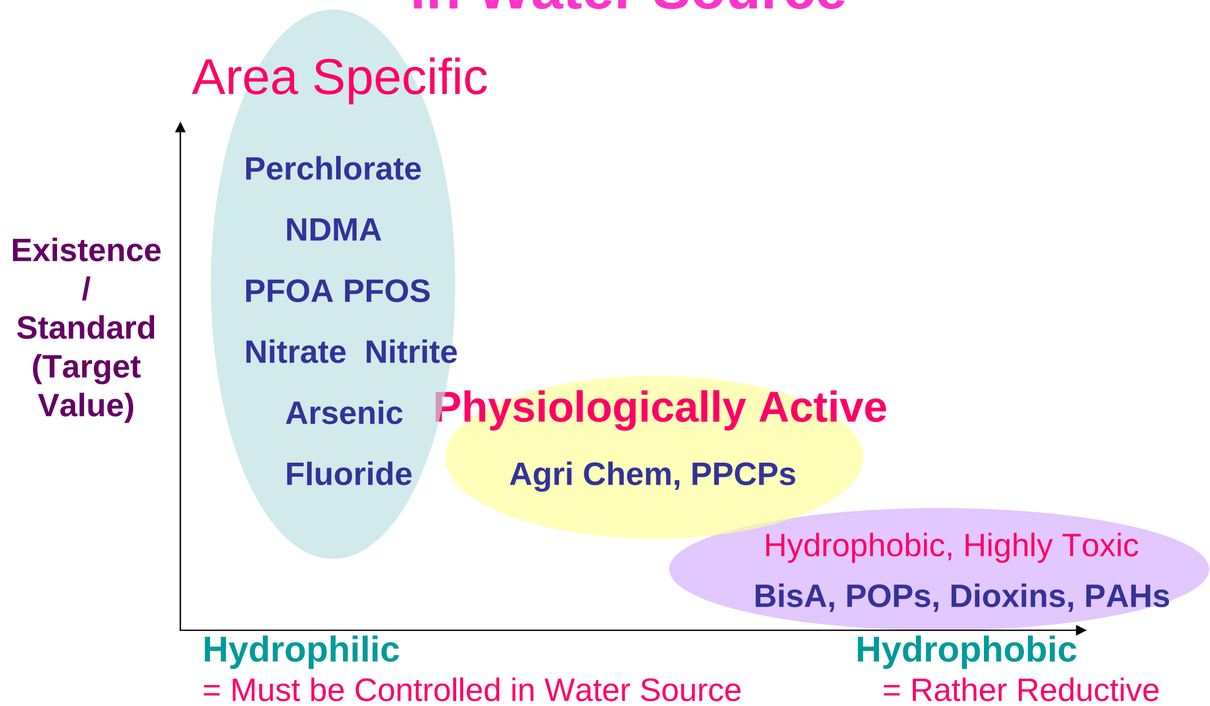
Priority Setting for Chemical Management in Water Source



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Emerging Contaminants in Drinking Water and Future Directions

- Few chemicals of large quantity
  → Many chemicals of small quantity
- Hydrophobic chemicals（Dioxin, Halogenated Organics) → Hydrophilic, polar chemicals (Chlorate, Perchlorate, NDMA)
- Intensive evaluation of exposure and reference value is needed !!

Strategic Approach is needed for management of Industrial Chemicals, Water Supply Chemicals including By-products, Natural Substances and PPCPs.

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