17. Endocrine Disrupting Chemicals

Presenter

Dr. Shoichi KUNIKANE, National Institute of Public Health

ENDOCRINE DISRUPTING CHEMICALS

Shoichi Kunikane

ABSTRACT

Endocrine disrupting chemicals(EDCs) are of great concern in Japan. We have been conducting researches on EDCs in drinking water. As the result, DEHP, DBP and BPA frequently occurred in raw water for drinking water supply. The maximum concentrations of DEHP, DBP and BPA were 0.53, 0.65 and 0.23 μg/l in raw water and 0.26, 0.18 and <0.01 μg/l in treated water, respectively. DEHP, BPA and NP could be removed by both conventional and advanced water treatment systems very well. Water pipes used for drinking water supply released DEHP, DBP, BPA and NP depending on the type of pipe material especially when they were newly installed, but the release did not last for a long time.

INTRODUCTION

Endocrine disrupting chemicals(EDCs) are of great concern not only among researchers but also among all people in Japan especially since the Environmental Agency disclosed their list, "SPEED 98" in 1998. Since then, we have been conducting studies on EDCs in water in order to collect information that can be used for estimating human uptake of EDCs through drinking water and assessing technologies for their effective control. The studies include their occurrence in raw and treated waters, behavior and removal in water treatment processes, and release from water pipes used for drinking water supply.

In this paper, the result of some studies on the occurrence of EDCs in raw and treated waters, removal and behavior of EDCs in drinking water treatment processes, and the release of EDCs from water pipes is reported and discussed.

OCCURRENCE OF EDCS IN RAW AND TREATED WATERS

The Japan Water Research Center(JWRC) conducted a surveillance on the occurrence of 68 chemicals including EDCs in raw and treated waters at 45 water treatment plants, 40 surface and 5 ground water treatment plants, all over Japan in 1999. Selected chemicals were ester phthalates, alkyl phenols, styrenes, organic tins, hormones,

Shoichi Kunikane: Department of Water Supply Engineering, National Institute of Public Health, Shirokanedai 4-6-1, Minato-ku, Tokyo 108-8638, Japan

pesticides and their by-products, and other related chemicals. Water sampling was done two times; first in July-October 1999 and second in October-December 1999. Both raw and treated waters were taken at the first sampling, but only raw water was taken at the second sampling. Samples were analyzed according to the "Provisional Manual for a EDCs Study" prepared by the Environment Agency.

As the result, out of 68 organic substances, 3 ester phthalates/adipates, 10 phenolic compounds, 5 pesticides and 1 organic chemical were found in raw waters, and 3 ester phthalates/adipates, 2 phnolic compounds, 3 pesticides were found in treated waters. Diethylhexyl phthalate was found most frequently both in raw water(88%) and in treated water(82%). Bisphenol A was also found frequently in raw water but seldom in treated water, which was probably due to degradation by chlorination in drinking water treatment. The maximum concentrations of DEHP, DBP and BPA were 0.53, 0.65 and 0.23 μg/l in raw water and 0.26, 0.18 and <0.01 μg/l in treated water, respectively. Such a result as described above was similar to that of a previous surveillance on the occurrence of 33 chemicals, including EDCs listed in the "SPEED '98," conducted in 1998.

REMOVAL AND BEHAVIOR OF EDCS IN DRINKING WATER TREATMENT PROCESSES

In order to know the removal and behavior of EDCs in drinking water treatment processes, such as coagulation/sedimentation, rapid sand filtration, ozonation and activated carbon filtration(BAC), we conducted an experiment using two advanced treatment pilot plants in Tokyo Metropolitan Water Supply and Osaka City Water Supply. The treatment flows are as follows:

Tokyo plant

1st line: Chlorination – coagulation/sedimentation - filtration
2nd line: Coagulation/sedimentation - sand filtration - ozonation - activated carbon filtration - sand filtration

Osaka plant

Coagulation/sedimentation - ozonation - sand filtration - ozonation - activated carbon filtration(BAC)

Four chemicals, such as diethylhexyl phthalate(DEHP), dibutyl phthalate(DBP), bisphenol A(BPA) and nonyl phenol(NP), were selected as target chemicals because they often occur in raw and treated waters in Japan. As their concentrations in raw waters of those pilot plants were usually very low, we sometimes spiked them into raw

Table 1 Occurrence of EDCs and other related chemicals in raw and treated waters

No.	Substance		QDL	Raw water				Treated water	
				Range detected	Detected/Measured			Range detected	Detected/ Measured
			mg/l	mg/l	Summer	Winter	Total	mg/l	Summer
1	Esteyl Phthalates	Diethylhexyl phthalate, DEHP	0.00005	ND~0.00053	42/45	37/45	79/90	ND~0.00026	37/42
2		Diethyl phthalate	0.00005	ND	0/45	0/45	0/90	ND	0/42
3		Di-n-buthyl phthalate, DBP	0.00005	ND~0.00065	13/45	8/45	23/90	ND~0.00018	5/42
4		Buthylbenzyl Phthalate	0.00005	ND	0/45	0/45	0/90	ND	0/42
5		Di-2-ethylhexyl adipate, DEHA	0.00001	ND~0.00002	1/45	0/45	1/90	ND~0.00002	2/42
6		Dicyclohexyl phthalate	0.00005	ND	0/45	0/45	0/90	ND	0/42
7		Di-n-propyl phthalate	0.00005	ND	0/45	0/45	0/90	ND	0/42
8		Dipentyl phthalate	0.00005	ND	0/45	0/45	0/90	ND	0/42
9		Di-n-hexyl phthalate	0.00005	ND	0/45	0/45	0/90	ND	0/42
10	Phenols	Bisphenol A	0.00001	ND~0.00023	14/45	15/45	29/90	ND	0/42
11		2,4-Dichlorophenol	0.00001	ND~0.00003	0/45	1/45	1/90	ND	0/42
12		Phenol	0.00001	ND~0.00005	1/45	18/45	19/90	ND~0.00001	1/42
13		4-Ethylphenol	0.00001	ND~0.00021	0/45	1/45	1/90	ND	0/42
14		2-tert-Buthylphenol	0.00001	ND~0.00002	1/45	0/45	1/90	ND	0/42
15		2-sec-Buthylphenol	0.00001	ND~0.00002	2/45	0/45	2/90	ND~0.00002	1/42
16		3-tert-Buthylphenol	0.00001	ND	0/45	0/45	0/90	ND	0/42
17		4-tert-Buthylphenol	0.00001	ND~0.00002	0/45	1/45	1/90	ND	0/42
18		4-sec-Buthylphenol	0.00001	ND	0/45	0/45	0/90	ND	0/42
19		4-Octyl phenol	0.00001	ND	0/45	0/45	0/90	ND	0/42
20		4-tert-Octyl phenol	0.00001	ND~0.00001	1/45	1/45	2/90	ND	0/42
21		Nonyl phenol	0.0001	ND	0/45	0/45	0/90	ND	0/42
22		4-n-Nonyl phenol	0.00001	ND	0/45	0/45	0/90	ND	0/42
23		2-Hydroxybiphenyl	0.00001	ND~0.00001	1/45	0/45	1/90	ND	0/42
24		3-Hydroxybiphenyl	0.00001	ND	0/45	0/45	0/90	ND	0/42
25		4-Hydroxybiphenyl	0.00001	ND~0.00001	0/45	1/45	1/90	ND	0/42
26	Stylenes	Octachlorostyrene	0.00003	ND	0/45	0/45	0/90	ND	0/42
27		1,3-Diphenylpropane	0.00001	ND	0/45	0/45	0/90	ND	0/42
28		cis-1,2-Diphenylcyclobutane	0.00001	ND	0/45	0/45	0/90	ND	0/42
29		trans-1,2-Diphenylcyclobutane	0.00001	ND	0/45	0/45	0/90	ND	0/42
30		2,4-Diphenyl-1-butene	0.00001	ND	0/45	0/45	0/90	ND	0/42
31		2,4,6-Triphenyl-1-hexene	0.00001	ND	0/45	0/45	0/90	ND	0/42
32		1c-Phenyl-4e-(1-phenylethyl) tetralin	0.00001	ND	0/45	0/45	0/90	ND	0/42
33		Styrene monomer	0.00001	ND	0/45	0/45	0/90	ND	0/42
34	Organo tins	Tributyltin	0.000005	ND	0/45	0/45	0/90	ND	0/42
35		Triphenyltin	0.000001	ND	0/45	0/45	0/90	ND	0/42
36	Hormones	Ethinyl estradiol	0.000002	ND	0/45	0/45	0/90	ND	0/42
37		17 β -Estradiol	0.000002	ND	0/45	0/45	0/90	ND	0/42
38	Major Pesticides	Benzoepin/Endosulfan	0.00005	ND	0/45	0/45	0/90	ND	0/42
39		Malathion	0.00001	ND~0.00003	1/45	0/45	1/90	ND	0/42
40		Methomyl	0.00001	ND~0.00013	3/45	0/45	3/90	ND~0.00001	1/42
41		Benomyl (as MBC)	0.0001	ND~0.0002	0/45	2/45	2/90	ND	0/42
42		Carbaryl	0.00001	ND	0/45	0/45	0/90	ND	0/42
43		Alachlor	0.00001	ND	0/45	0/45	0/90	ND	0/42
44		Trifluralin	0.00005	ND	0/45	0/45	0/90	ND	0/42

Note) "ND" means not detected above a quantitative detection limit.

Table 1 Occurrence of EDCs and other related chemicals in raw and treated waters (continued)

No.		Substance	QDL	Raw water				Treated water	
				Range detected	Detected/Measured			Range detected	Detected/ Measured
			mg/l	mg/l	First	Second	Total	mg/l	First
45	Pestices of Prohibited Commercial Use or Manufacuring	Hexachlorobenzene	0.00005	ND	0/45	0/45	0/90	ND	0/42
46		o,p'-DDT, p,p'-DDT	0.00005	ND	0/45	0/45	0/90	ND	0/42
47		Ardrin	0.00005	ND	0/45	0/45	0/90	ND	0/42
48		Endrin	0.00005	ND	0/45	0/45	0/90	ND	0/42
49		Dieldrin	0.00005	ND	0/45	0/45	0/90	ND	0/42
50		Heptachlor	0.00005	ND	0/45	0/45	0/90	ND	0/42
51		trans, cis-Chlordane	0.00005	ND	0/45	0/45	0/90	ND	0/42
52		Methoxychlor	0.00005	ND	0/45	0/45	0/90	ND	0/42
53		Hexachlorocychlorohexane, HCH	0.00001	ND~0.00002	1/45	0/45	1/90	ND~0.00001	1/42
54		Amitrole	0.00005	ND	0/45	0/45	0/90	ND	0/42
55		2,4,5-Trichlorophenoxyacetic acid	0.00005	ND	0/45	0/45	0/90	ND	0/42
56		1,2-Dibromo-3-chloropropane	0.00001	ND	0/45	0/45	0/90	ND	0/42
57		Nitrofen	0.00005	ND	0/45	0/45	0/90	ND	0/42
58		Pentachlorophenol, PCP	0.00001	ND~0.00004	2/45	2/45	4/90	ND~0.00001	1/42
59	No-intended By-products	tarns-Nanochlor	0.00005	ND	0/45	0/45	0/90	ND	0/42
60		p,p'-DDE, o,p'-DDE	0.000001	ND	0/45	0/45	0/90	ND	0/42
61		p,p'-DDD, o,p'-DDD	0.00001	ND	0/45	0/45	0/90	ND	0/42
62		Heptachlor epoxide	0.00005	ND	0/45	0/45	0/90	ND	0/42
63		Oxychlordane	0.00005	ND	0/45	0/45	0/90	ND	0/42
64	Other organics	Benzo(a)pylene	0.00001	ND	0/45	0/45	0/90	ND	0/42
65		Polybrominated biphenyls	0.00001	ND	0/45	0/45	0/90	ND	0/42
66		4-Nitroroluene	0.00001	ND	0/45	0/45	0/90	ND	0/42
67		n-Butylbenzene	0.00001	ND	0/45	0/45	0/90	ND	0/42
68		Benzophenone	0.00001	ND~0.00002	1/45	2/45	3/90	ND	0/42

water(at Tokyo plant) or the water after sedimentation and before ozonation(at Osaka plant) at a concentration of 1 or 5 μg/l for each chemical. The experiment was done several times at each plant in 1999-2001.

The result has shown that all of these chemicals can be removed well by both conventional and advanced water treatment systems, except for DBP in the case of a conventional water treatment system by chlorination, coagulation/sedimentation and filtration. DEHP was removed by coagulation/sedimentation, rapid sand filtration and activated carbon filtration, but not by chlorination or ozonation. DBP was removed by rapid sand filtration, without chlorination before that, and activated carbon filtration. Figure 1 shows the removal of DEHP and DBP by rapid sand filtration. Rapid sand filtration could remove DEHP very well, but the reason is no clear. Contrarily, BPA and NP were removed by chlorination and ozonation. Figure 2 shows the removal of BPA and NP by ozonation.

Bisphenol A and nonyl phenol could easily be reduced by chlorination. We obtained the same result in a previous laboratory experiment. However, we have found in another laboratory experiment that chlorination by-products are formed as the result, and a bisphenol A solution after chlorination has an estrogenic activity higher than that of the original bisphenol A solution. We also found, in this pilot plant experiment, the formation of 2,2',6,6'-bisphenol A, one of the chlorination by-products of bisphenol A which has a high estrogenic activity.

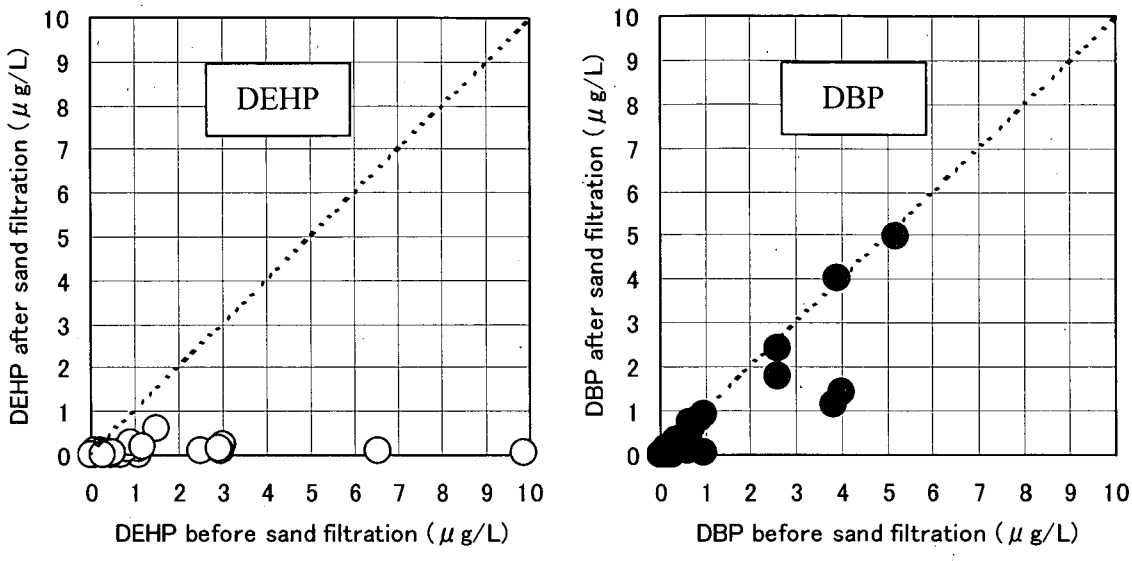

Figure 1 Removal of DEHP and DBP by rapid sand filtration

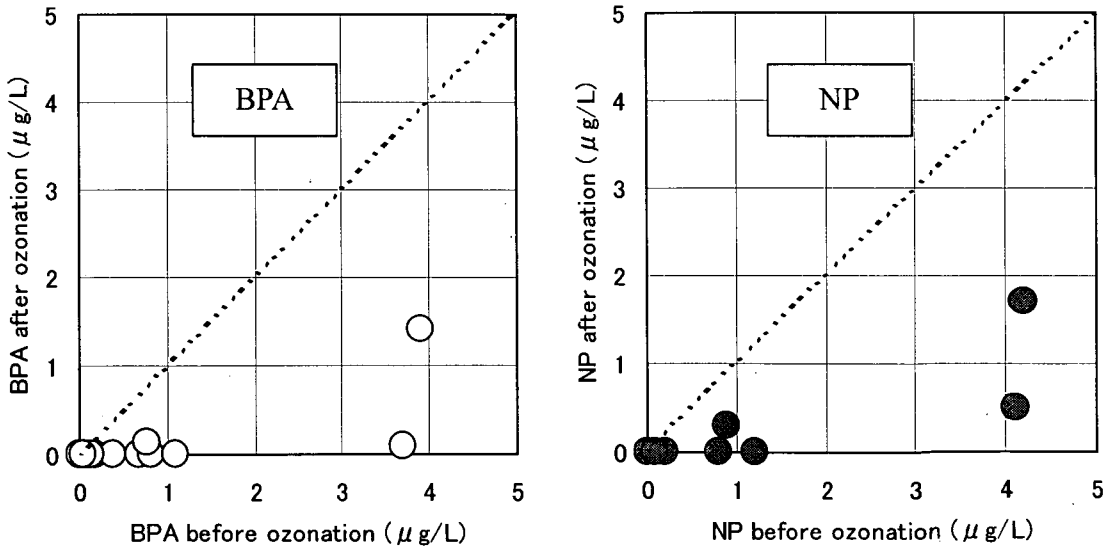

Figure 2 Removal of BPA and NP by ozonation

RELEASE OF EDCS FROM WATER PIPES USED FOR DRINKING WATER SUPPLY

An examination has been conducted using seven types of virgin water pipes in order to obtain information on the long-term profiles of EDC release. The target chemicals were DEHP, DBP, BPA, and NP. Pipes used were two brands of DIP, SGP-V, SGP-P, PE, VP, PEP and XPEP at a diameter of 20-75 mm produced by different manufacturers for each. The EDC release test was repeated several times with a certain interval during a period of two years. Otherwise the pipes were connected to each other in two parallel identical lines and fed with drinking water containing residual chlorine at a concentration of about 1 mg/l continuously. The contact of pipes with test water, pH at 7.0, hardness at 45 mg/l, alkalinity of 35, and residual chlorine at 1.0 mg/l, in the EDC release test was for 16 hours at 23 ± 2 degrees centigrade. We also defined a limit of release determination for each of DEHP, DBP, BPA and NP at 0.4, 0.4, 0.01 and 0.08 μg/l, respectively, based on a result of quality assurance measurements.

As the result of a release test at the beginning, DBP was released from almost all pipes tested, but each of DEHP, NP and BPA was released only from a limited number of pipes tested. There was a general trend of decrease in the release of these four chemical compounds. None of these compounds were released from any pipe tested after one year. However, the release of BPA and DBP were found after one and half years and after two years, respectively. The maximum concentrations of DEHP, DBP, BPA and NP were 2.1 μg/l (11.0 $\mu g/m^2$), 2.2 μg/l (11.0 $\mu g/m^2$), 0.54 μg/l (2.7 $\mu g/m^2$) and 2.3 μg/l(12.0 $\mu g/m^2$), respectively. All of the maximum values were found for virgin pipes, i.e. after 0 months.

CONCLUSIONS

The conclusions of our studies on EDCs in drinking water are as follows:

1. DEHP, DBP and BPA frequently occurred in raw water for drinking water supply.
2. The maximum concentrations of DEHP, DBP and BPA were 0.53, 0.65 and 0.23 μg/l in raw water and 0.26, 0.18 and <0.01 μg/l in treated water, respectively.
3. DEHP, BPA and NP could be removed by both conventional and advanced water treatment systems very well. The profiles of removal of DEHP, DBP, BPA and NP in water treatment processes were different from each other depending on their chemical property.
4. Water pipes used for drinking water supply released DEHP, DBP, BPA and NP depending on the type of pipe material especially when they were newly installed, but the release did not last for a long time.