Research Development of Endocrine Disrupting Chemicals (EDCs) in Water in China

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More and more importance has been attached to the problem of endocrine disrupting chemicals (EDCs) since 1960s. This article elaborates the recent research progress of EDCs in water and the trends in the near future in China.

Key words: Endocrine disrupting chemicals; Source water; Alkylphenols; Phthalates; Atrazine

INTRODUCTION[1]

Till now there are about 20 billions kinds of man-made synthetic compounds, among which 70-80 thousands kinds are often used. Their adoption pushes the society forward and makes men's life convenient. But during their production, uses and wrong disposes, they may do great harm to environment, even causing harzards or environmental risks. Reviewing large amount of research data since 1960s, it is found that certain kinds of chemicals not only is carcinogenic, teratogenic or mutagenic, but also may disrupt the reproductive systems of human-beings and animals. It will threaten our generation's future living and species' multiplying. Therefore, scientists are paying more and more attention to the screening of such kinds of chemicals and it has become a hot-point problem. Such kinds of chemicals are called "endocrine disrupting chemicals" (EDCs) or "environmental hormone".

Endocrine disrupting chemicals do their harm in three main aspects. The first is that they disturb organism's reproduction and growth, depressing productive abilities or leading to abnormal physiological phenomena. The second is that they may lower immune abilities, causing more cancers. The last is that they could affect development of nerve system, impairing it or disrupting its endocrine function.

The possible action mechanism is as follows. After their entering organism, endocrine disrupting chemicals can mimic the hormones that serve as the messengers regulating the endocrine system, and compete with its own hormone to combine with the receptors of target cells. This will cause obstruction and bring bad effect on endocrine system.

Because EDCs are diversiform, complex and in low concentration, relevant detection methods must be sensitive and large sample amount is required, which may vary from 1 to 10 litres according to water's pollution extent and specific kinds of studied chemicals.

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Two main measuring methods recently used are instrumental and biological techniques.

Instrumental techniques include GC, GC/MS, and LC/MS. Samples are commonly pretreated before analysis, including extraction (for example, liquid-liquid extraction and solid phase extraction), enrichment, elution and clearing up. Some methods have been established for the detection of NPnEO and their biodegradation products such as nonylphenol (NP), alkylphenols and 16 kinds of organic pesticides (including atrazine, nitrofen, lindane, chlordane, malathion, etc.) which are suspicious EDCs. These methods are rather effective in detecting the target compounds.

Biological techniques are used to screen EDCs and study the disrupting effects of the screened chemicals on the growth and reproduction of organisms. There are some other biological methods, for example, tests *in vitro* and tests *in vivo*. Tests *in vivo* mainly include estrogen receptor (ER) test and androgen receptor (AR) test. The two commonly used ER tests are MVLN and two-hybrid yeast system.

In 1998, Japan surveyed EDCs in different water bodies and the results suggested that there were eight kinds of EDCs in water, such as phthalates, phenols (including alkylphenols, high-polarity bisphenol-A and chlorophenols), entrogens, epoxychloropane, organic pesticides (including herbicides and insecticides). Since EDCs enter people's body mostly through food and water, it is necessary to know the bad effects of such kinds of chemicals on human beings and their content in source water, finished water and distribution water. Studying water treatments' effect on EDCs and how to control them has become one of the water treatment engineers' important tasks.

The following is the recent work on this theme in China.

RESEARCH DEVELOPMENT OF EDCS IN WATER IN CHINA

Bad Effects of EDCs on Organisms

Studying the data of 11 726 person-time sperm samples from 1981 to 1996, researchers found that sperm number was decreased by 20%, the ratio of active sperm was decreased by 8% and that of normal-form sperm 7%. The above data were all negatively relevant and meaningful in statistics[1]. It indirectly demonstrates that more and more organic pollutants, particularly EDCs, are likely to affect the sperm quality and reproduction of human-beings.

Androgen toxic chemicals in drinking water-chloroform, nitrotoluene and phthalates and so on could greatly affect enzymes' activities which are indirectly relevant with testosterone synthesizing or sperm producing energy. ATPase enzyme has direct influence on sperm's growth-lowing sperm activity, sperm density and serum testosterone content[2].

Both *in vivo* and *in vitro* experiments showed[3] that the death rate of spermatogonia rose while the proliferation rate dropped significantly ($P<0.05$) with the increase of 2-bromopropane concentration. Histological examination results were that 2-bromopropane impaired spermatogonia before it had any toxic effects on other organs. Spermatogonia was likely to have pyknotic nucleus or appear necrosis. So it is concluded that spermatogonia is probably the target cell of 2-bromopropane and *in vitro* new spermatogonia culture system could be adopted as one assistant method to detect or screen exogenous reproduction-toxic chemicals such as EDCs.

Mutation effect of 12 kinds of alkyl-hydroxybenzene which are potential EDCs, was investigated by Ames test[4], using TA97, TA98, TA100 and TA102. Results showed that except 2,4-dichlorophenol, the other alkyl-hydroxybenzenes have positive response to the TA98. Among them, nonylphenol, 4-octanylphenol and 2,6-dimethylphenol have stronger positive response and are suspected to be strong-mutagenic chemicals. And the main type of gene mutation is base-pair frame-shift.

EDCs Distribution in Surface Water and Their Characteristics

Kinds of EDCs distribution in large water fields Yeru Huang and her colleagues have made surveys in different waters in China-Huanghai, Bohai, Donghai Seas, Yangtze River and others. Initial results showed that residue of organic chlorine pesticides is still serious in certain offing sea area. For example, the total content of four kinds of lindane is around 100 ng/L. N-butylphenol, nonylphenol, bisphenol-A, penlachlorophenol and 2,4-dichlorophenol are all existing in the surveyed sea areas or inland rivers. We should pay more attention to high concentration phthalates in sea water. Where there are more ships, there are relatively larger amount of organotins in the area, especially tributyltin oxide and triphenyltin. The concentration of organotins in Bass or sea water is shown in Table 1.

TABLE 1

Concentration of Organotins in Bass (ng/g) and Sea Water (ng/L),1997

Different Places	Bass (ng /g)			Sea Water (ng /L)		
	Shanghai	Qindao	Tianjin	Shanghai	Qindao	Tianjin
Tributyltin	6.8	7.4	10.1	34.9	37.1	284.9
Triphenyltin	16.5	22.4	24.4	23.3	8.9	8.9

From Table 1, we could see that the concentration of triphenyltin is higher than that of tributyltin in Bass but contrary in sea water. Because Bass sample from Shanghai was bred aquatic product and the concentration in Bass from different places was close, it may be concluded that no serious organotins enrichment occurs in Bass from any of the studied sea area.

NPEO and NP in Yangtze River and Jialingjiang River.[5] Yangtze River and Jialingjiang River are the two main rivers in Chongqing, providing water for agriculture, industry, civil use and drinking. Five points were chosen and water was sampled in different seasons of different water temperatures to detect nonylphenol ethoxylates（NPEO）and its biodegradation products nonylphenol (NP). Experimental results showed that the concentration of NPnEO in Yangtze River varied from 3.5 to 100 μg/L and NP changed between 0.05 and 7.5μg/L，similar to that of Japan but higher than that of developed countries such as America. In Jialingjiang River, the NPnEO content was lower than that in Yangtze River but NP was somewhat higher. NPnEO concentration in Yangtze River approximates to Gauss distribution and in Chongqing the commonly used NPnEO’s polymeric number varies from 9 to 15.

Phthalates (PAEs) enrichment behavior in waters microlayer[7]. PAE is the main component of plastic which is widely used as food package materials, containers, medical materials, man-made leather, etc. Natually, its consumption increases year by year. Plastic is difficult to be broken down naturally and PAE of it is about 30%-50%, so PAE becomes the common pollutant in water.

Enrichment behavior of dibutyl phthalate(DBP), di-(2-ethyl)hexyl phthalae(DEHP) and anionic surfactant in the waters surface microlayer were studied. Results of field analysis showed that the phthalates enriched in the microlayer of small blocked lakes and enrichment factor ranged between 1-11.Physical-chemical properties of waters and collecting methods have great effect on enrichment. Study in indoor microcosm revealed that DBP and DEHP were enriched in the surface microlayer of the microcosm with the enrichment factors 2.81 and 1.98, respectively. At the same time, algae, particulate and humic acid also gathered there. The enrichment of phthalates decreased with the concentrations of surfactant and humic acid. Study on the enrichment dynamics of anionic surfactant showed that if the microlayer of waters was destroyed, it needed a long time to reach the enrichment equilibrium again.

EDCs Pollution in Source Water and Finished Water

City C in Southwest China[2]. Analysis of organics in the source water and drinking water from three different waterworks were carried out by GC/MS methods. All the three kinds of source water were from a same river, but not the same sect. The Sixth plant was on the upstream, far away from the city. The second plant and the fifth plant were both on the downstream. Water treatment process in three waterworks was essentially of the same type.

More than 230 kinds of organic pollutants have been found in the source water and drinking water of the city. Predominant organic compounds include phthalate esters, PAH, fattly acids, amines, heterocyclic compounds, alkane, etc. Seven kinds of them are parts of preferentially controlled pollutants in China. The highest content of organic chemicals was in samples from the Sixth plant and the lowest in samples from the Second plant. Nonylphenol, 4-methylphenol and other alkylphenols were detected in the source water of the Second plant, and 4-nonylphenol and 4-ethylphenol were found in its finished water. In the source water and finished water of the sixth plant 2-nonylphenol and other kinds of alkylphenols were detected, and benzopyrene was found in the finished water. Six kinds of phalates were found in all the three kinds of source water and finished water. Among them, the content of dibutyl phthalate(DBP) was the highest, and diethylhexyl phthalate (DEHP) and diethyl phthalate were both preferentially controlled pollutants of USEPA.

City H in Southeast China[8]. The water source of waterplants in this city is Qiantang River and its tributaries. Samples were taken from ten water plants in the city or nearby and dibutyl phthalate was detected in the samples from each source water and finished water. The highest content was 0.076 mg/L. Diethylhexyl phthalate (DEHP) was detected in five plants' samples and its highest concentration was 0.017 mg/L. However, dimethyl phthalate and diethyl phthalate were not detected.

TABLE 2

Concentration of Dibutylphthalate in Source Water and Finished Water（mg/L）

Waterworks	A	B	C	D	E	F	G	H	I	J
Source Water	0.021	0.032	0.017	0.003	0.020	0.014	0.013	0.001	0.014	0.033
Finishedwater	0.076	0.011	0.020	0.008	0.005	0.013	0.024	0.014	0.009	0.027

From Table 2, we can see that dibutyl phthalate is significantly removed by B, E and I water treatment facilities, and their removing rates are 65.6%, 75% and 35.7% respectively. In the finished water of the four plants—A, D, G and H, the concentration of dibutyl phthalate is significantly higher than that in the source water.

It is clear that different water treatment processes will greatly affect PAEs content in finished water. Studying on effects of different water processings on PAEs is meaningful. Only after we know the reason could we find the key to this problem-controlling and resolving it.

City B in North China[9]. Yongding River, which flows by Guanting Reservoir and San Jiadian Reservoir, is the water source of Chengzi waterworks whose capacity is 43 000m^3/day.

In source water there are 52 kinds of organic compounds detected. Thereinto 29 kinds of chemicals are mutagenic, carcinogenic or endocrine-disrupting, such as atrazine, five phthalates and alkylphenols. In the effluent from conventional process (not disinfected by chlorine), there are 38 kinds of organic compounds among which 19 kinds are toxic, including atrazine, phthalates and alkylphenols.

The most recent study shows[10] that atrazine residue in Guanting Reservoir-main surfacewater source of Beijing is about 0.67-3.9μg/L, lower than the limited concentration 3 μg/L in the standard. But long term effects of lower concentration of atrazine-one kind of EDCs, will threaten human being' s immune system and nerve system. So it is necessary to carry out source controlling and minimize the amount of such kind of dangenrous compounds entering water as possible as we could. No atrazine has been detected in samples from Miyun Reservoir, or it is under the detection limit of 0.01 μg/L.

Effects of Water Treatment Process on EDCs

Nonylphenol and its precursor NPEO[11]. Field experiments showed that more than 90 ％ long-chain NPEO can be removed by traditional water treatment process (including flocculation, sendimentation, filtration and disinfection by chlorine), but only about 60％ of NP which is a stable broken-down product of NPEO could be removed from water. Flocculating adsorption and chlorine-disinfection oxidization are the possible reason for NP removal.

Effects of biological pretreatment on EDCs[9]. Original treatment process in Chengzi waterworks includes clarification, filtration, activate-carbon adsorption and chlorination disinfection. Analyzing organic pollutants in effluents of original treatiment process, biological pretreatments and their combinations by GC/MS, we found that the ceramic granular biofilter was superior to other cells in controlling kinds of organic compounds or minimizing carcinogenic, teratogenic or mutagenic substances in water. For example, atrazine existed in source water and effluent from conventional process, but in effluents from ceramic granular biofilter or combination of coagulation, sendimentation and ceramic granular biofilter, no atrazine was detected or under detection limit. It is suggested there is no atrazine in effluent from biological pretreatments either and that microorganism has certain ability to degrade such kinds of compounds. However, pretreatment isn' t distinctly effective on removing phthalates or alkylphenols.

Effects of disinfection on nonylphenol and bisphenol A[6]. The results based on the yeast two-hybrid systems showed that while the chlorine disinfection by-products of bisphenol A elicited estrogenious agonist, those of nonylphenol elicited estrogenious antagonism. On the other hand, certain test identified that bisphenol disappeared during the period of chlorine disinfection but endocrine disrupting effects of its disinfection by-products-polyhydroxybenzene were much stronger than those of bisphenol itself. Such a problem is worth great attention.

RESEARCH IN THE NEAR FUTURE

What we should do in the near future is as follows:

A. To find out the status of production, use, disposal of certain endocrine disrupting chemicals and their amount entering waters in China.

B. To establish effective and mature methods for detecting main EDCs in water, including instrumental and biological methods.

C. To investigate kinds and content of EDCs in source water and their distribution in water.

D. To study effects of different water treatment processes on main kinds of EDCs and their characteristics along the processes.

E. To provide valid controlling strategies such as source control or choose best combination of treatment units to remove EDCs.

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