

## Research progress of Endocrine Disrupting Chemicals in water

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**Abstract.** Endocrine disruptor chemicals (EDCs) is a kind of xenobiotics have the functions of carcinogenic, teratogenicity, accumulation and biological magnification. In recent years, with all kinds of chemicals and a lot of use of pesticides, the amount and type of EDCs in river water increased apparently, it constitutes the great threat to the ecological environment and human health in China. Based on the systematic analysis of the definition, types, characteristics and harmfulness about EDCs, conclude the detection technology and biodegradation methods research of EDCs in water studied by scholars domestic and abroad in recent years, in view of the insufficiency of Songliao basin EDCs research, combined with the existing research situation put forward the future research direction of EDCs in Songliao basin.

### Introduction

EDCs mainly refers to exogenous substances that present in the environment can interfere with the synthesis, release, transport, binding, action, or remove of endogenous hormones, in turn affecting the stability of the body's internal environment, developmental and behavior[1]. Because of EDCs are difficult decomposed, not only cycle in the food chain, but also walk following the ecological cycle of nature, affecting the normal function of the animal reproductive, endocrine, nervous and immune system. Studies have shown that EDCs impact animals' reproduction by acting on the hypothalamus-pituitary-gonadal axis of the endocrine system; also acts on the hypothalamus - pituitary - thyroid axis, influence the process of thyroid hormone's synthesis, transport, binding, etc. destabilizing the thyroid hormones in the environment to harm the growth and development of person[2]. Meanwhile, EDCs can cause the immune ability of the organism to make thymus indentation and the immune function of the organism changes by reducing or suppressing. Therefore, enhancing the detection technology of EDCs in water, developing efficient and economical method of EDCs removing and degradation, it is significant for the mitigation of water ecological problems and the promotion of sustainable development of water environmental health. This article is based on systematic analysis of EDCs definition, types, characteristics and dangers, summarized recent research about detection techniques and degradation methods of EDCs in water, for the shortcomings of research Songliao basin EDCs, thereby improving water contaminant detection system of Songliao basin.

### Types and characteristics EDCs

US Environmental Protection Agency select out 67 kinds of "Endocrine Disrupting Chemicals" from 86,000 kinds of products and chemicals which endangering humans and creatures in 1998. The nature of these compounds vary greatly, not only contain refractory dioxins, polychlorinated biphenyls, organochlorine pesticides, phthalic acid ester, but also another labile polar herbicides, insecticides, and organometallic compounds detergent degradation, etc.. So far, the species of chemical substances around the world have registered more than 20 million kinds, and increase more than 100,000 kinds of new substances each year. About 200 kinds of it are suspected of affecting human health, about 70 kinds of chemicals are suspected effect the endocrine system of animals and humans[3]. US Environmental Protection Agency lists a total of 60

species, the US Centers for Disease Control and Prevention lists 48 species, Japanese lists a total of 65 species, Korean lists 66 species, the European Union lists 118 species. With further research and identification of toxicity, EDCs species there will also be amended and Increase or decrease.

EDCs has the following characteristics: (1) endocrine disruptors are compounds from various sources, including natural estrogens, drugs (such as birth control pills), estrogen replacement, other steroids, various industrial chemicals such as dioxins, polychlorinated biphenyl can enter into the water with the rain and sewage, causing water pollution;(2) Most endocrine disruptors have lipophilic, resistance to chemical and biological degradation, persist in the aquatic environment and bioaccumulate through biological enrichment and the amplification of the food chain, witch is not easy to exclude in the human body.(3)Human beings contact toxic and hazardous pollutants universally , the human body more or less sucked endocrine disruptors and persistent organic pollutants and heavy metals almost. Due to persistent and lipophilic organic pollutants can accumulate in freshwater fish and produce biomagnification through the food chain and affect the human body. Endocrine disruptors hormone is exogenous substance, has the function of hormone, but it is not similar with natural hormone of living body and other or steroid hormone in the chemical structure, and the chemical structure of these xenobiotics is also different. Even though the concentrations of endocrine disruptors in the water was low, there will be a large number of molecules combine with person or other biological receptors in the body and cause harm.

### **The research work of EDCs**

Back in the 1980s, people found the phenomena that feminized males, development abnormal and reproductive disorders and other appeared in the United States, Florida, southern England, and wildlife in the western suburbs of Tokyo. And until the 1990s, environmental problems caused by endocrine disruptors was widespread concern in the world, especially civil society organizations and international organizations of Europe and Japan and other countries, governments . Colborn describing the harmful caused by hormone function compounds on biological endocrine disruptors systems in the "Our stolen future" book, such as feminization, decreased fertility and developmental defects, and may lead to the extinction of the population ultimately, causing widespread concern around the world.

Since the 1990s, the environmental impact of environmental endocrine disruptors generated widespread concern of the international community.EU, US, Japan, Organization for Economic Co-operation and Development and the World Wildlife Fund and other organizations, including government and non-governmental organizations have begun to study it and treat it as the key research areas. The study includes the establish the selection method for detecting environmental endocrine disruptors and to establish a priority list, Identify and study the harmful and its mechanism of environment endocrine disruptors on humans and wildlife, assessing and managing risk of environmental endocrine disruptors . Governments put forward the strategic plan and develop relevant policies and regulations to control EDCs.

### **The research situation of EDCs in China**

In recent years, China is also beginning to pay attention to EDCs research, but more developed countries, China's research is still weak in this area relatively , needs to learn international advanced technology and experience. Atrazine, as a general EDCs of China, began to be used as early as the 1980s, has been widely promoted and widely used in North China and Northeast China until the 1990s.Ren Jin investigated Zhangjiakou region and Guangting Reservoir watershed water atrazine and its degradation products, less toxicity of atrazine and its metabolites were detected in surface water from pesticide plant outfall in Xuanhua, most beyond of  $3\mu\text{g}/\text{L}$  in surface water quality standards, and found atrazine and its degradation products in the deep well of.

Endocrine disruptors can affect the body's normal endocrine function, carcinogenic, teratogenic, bioaccumulation role. Therefore, the removal of endocrine disruptors is very important for the safety of

drinking water. While the international community has made various studies, but endocrine problems interfering chemicals has just begun to attract attention. China's research in this area, especially in the field of drinking water treatment research, still in its infancy. In short, the screening, analysis and evaluation as well as the removal of endocrine disruptors is a long-term work, it covering many fields of science, in order to further understand the mechanism of action within the shunt disruptors and found effective removal methods must go through a long period of time.

### Detection techniques and degradation methods of EDCs

Currently, the detection of environmental endocrine disruptors including chemical analysis, instrumental analysis and biological testing, instrumental analysis detection method is generally applicable to known environmental endocrine disruptors, biological testing is generally applicable to a variety of environmental endocrine disruptors comprehensive toxicity testing [4].

Chemical analysis and detection methods of phenolic EDCs are applied least. Drinking water sources in the EU Directive (75/440 / EEC, ended in December 2007) proposed a method to detect all phenolic EDCs, namely the use of potassium ferricyanide (Potassium Ferricyanide) of color, through 4 - amino antipyrine (4-aminoantipyrine) to determine the total concentration of phenol, but poor of immunity and sensitivity, targeted not strong, so do not get the promotion, and gradually replaced by the instrument analysis[5].

The traditional instrumental analysis are gas chromatography and mass spectrometry (GC-MS), however, the analysis of the low concentration of EDCs, GC-MS method has some limitations, such as the presence of the former pre-column derivatization and column transformation and other issues. HPLC method is also commonly used to analyze environmental endocrine disruptors, generally using UV detector (UVD), fluorescence detection (FLD), chemiluminescence detection (CL) or electrochemical (ED) and other detection methods. Wherein, FLD, CL and ED have high sensitivity, UVD detector lower relatively. These detection methods can't analyze the structure of EDCs, and often need LC-MS system [6].

The method of biological test is fast, economical, efficient, and can be directly measured the activity of endocrine disruptors in environmental samples, the characterize the toxicity of environmental endocrine disruptors, and therefore become a hot topic in recent years in environmental endocrine disruptors detection field. At present, more mature environment estrogenic activity identification methods are: (1) competitive inhibition of estrogen receptor; (2) (Yeast Estrogen Screen, YES); (3) lactoferrin mRNA law; (4) vitellogenin law; (5) animals experiment. In addition, some scholars have also developed a Hershberger test method and restructuring AR gene and recombinant yeast hybrid method to evaluate the effect of androgens.

### EDCs degradation method

At present, most of the researches on the removal of EDCs concentrated in conventional wastewater treatment, activated carbon adsorption, advanced oxidation and catalytic oxidation, biodegradation methods. Although activated carbon adsorption and advanced oxidation has good removal, but has higher operating costs, and can cause secondary pollution. By contrast, the biological research become hot recently because of incomparable advantages.

Liu Jian, who checked the horizontal subsurface flow constructed wetlands for municipal sewage in the eight kinds of endocrine disruptors removal. The results show that: the hydraulic loading is 0.17 m<sup>3</sup>/d, under the case of HRT is 4.6 d, estrone (E1), estriol horizontal subsurface flow constructed wetlands (E3), bisphenol A (BPA), Helsinki phenol (OP), 17 $\beta$ - estradiol (E2), 17 $\alpha$ - estradiol (17 $\alpha$ -E2), 17 $\alpha$ - ethinyl estradiol (EE2) average removal rates were 81.4%, 39.3%, 73.9%, 44.1%, 69.7%, 82.2%, 65.2%. Among them, 4-n-nonylphenol (4-n-NP) in wetland effluent is not detected.

Zhouying Jun used simulative sewage, under the same operating conditions, compare the study of the MBR and SBR for the removal of seven kinds of typical endocrine disruptors activity. The results showed that adding tests does not affect endocrine disruptors and stable operation of SBR and MBR; for target 17 $\beta$ -

estradiol (E2), estriol (E3), bisphenol A (BPA), 4-nonyl phenol (4-NP) and 4-octylphenol (4-OP), MBR and SBR no significant difference to their removal; but MBR of nonylphenol polyoxyethylene ether (NP-n-EO, n average about 1.5) and 17 $\alpha$ -ethinylestradiol (EE2) removal of a better and more stable than the SBR. In addition, the removal of endocrine activity is also better than the SBR.

Although our EDCs research of drinking water sources started lately, but according to the survey data having been carried out show that our drinking water sources was detected higher concentrations of endocrine disruptors, polluted seriously, it is not optimistic. The preliminary findings of EDCs in Harbin section of the Songhua River show that 13 kinds of typical EDCs almost were 100% detected, including estriol (E3), estradiol (E2), estrone (E1), B ethinylestradiol (EE2) and diethylstilbestrol (DES) 5 estrogenic substances; dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP) phthalate and di (2-ethylhexyl) ester (DEHP) 4 phthalates; 4-n-nonylphenol (4-n-NP), nonylphenol (NP) and 4-tert-branched - octylphenol (4-t-OP) three kinds of alkylphenol [7].

Shao Xiaoling and others survey the raw water of Songhua River Basin plant by solid phase extraction - high performance liquid chromatography, 13 kinds of endocrine disrupting chemicals (EDCs) conventional water purification process each processing unit in the water pipe network. The results show that expect steroid estrogen substances were not detected in the water pipe network, other water samples were detected at concentrations of 4 ~ 44 ng / L; 4 phthalate esters (PAEs), bisphenol A (BPA), and three kinds of alkylphenols (APs) detected nearly 100% in all water samples at a concentration of 2 ~ 163760ng / L, which dibutyl phthalate (DBP) and phthalic bis (2-ethylhexyl) phthalate (DEHP) based. The study also found that, although there are individual EDCs effluent concentrations higher than the influent concentration, but coagulating sedimentation process to remove EDCs play the dominant role in the water, the average removal rate was 63%; sand filtration and chlorine disinfection process effluent unstable only partial removal of EDCs play a role to some extent. In addition, the factory after delivery network administered by the vast majority of the water in which EDCs levels increased, indicating that except the way of EDCs entering the pipe network water pollution, there is an important way that the corresponding pollutants in water pipes dialysis.

Chang Han clarify the status of the Songhua River water pollution of endocrine disruptors, using Solid Phase Extraction - GC-MS / recombinant yeast sampling and analysis 11 typical section of the Songhua Jiang comprehensive. The results show that: the concentration of EDCs in the river is 6.59 ~ 30.97 ng / L, average 17.23 ng / L, the largest concentration appeared position Darien River outfall, estrone and estradiol estrogen is one of the greatest contribution hormones, its concentration in the range of 1.54 to 6.34 and 1.86 ~ 20.78 ng / L, mainly from urban sewage; all sampling points are detected nonylphenol, octylphenol and bisphenol A, its concentration ranges were 236.3 ~ 1067.9, 3.07 ~ 256.10 and 13.0 ~ 206.5 ng / L, mean 512.8, 34.1 and 52.8 ng / L, which was higher than the concentration of estrogen, mainly from domestic sewage and industrial wastewater; estrogen Songhua River water body activity was 0.50 ~ 26.16 ng / L, the maximum in Kazakhstan under the sampling point, sewage is an important source of estrogenic activity, other sampling points EEQ mass concentrations were less than 3.60 ng / L, its concentration in the river at home and abroad the same level of contamination, but there is potential ecological security issues.

## Summary

(1) Increase research efforts, improve relevant standards.

Increase capital investment, combined with some excellent research results as well as the international advanced detection technology, extensive research work endocrine disruptors. At present, China is more concerned about the source of endocrine disruptors, distribution and damage, while the toxic effects of endocrine disruptors mechanism, environmental capacity, pathogenic concentration, exposure pathways and the effects of research relationships rarely, is not conducive to the endocrine disruptors scientific evaluation of risks and scientific control, so strengthened in the future in-depth research in this area is necessary, establish a reasonable list of endocrine disruptors, formulate and improve relevant standards.

(2) Increase the water reform process.

At present, China mainly conventional water treatment process technology, advanced treatment process, membrane treatment process and biological treatment processes. Our water purification process plant using conventional technology, using "coagulation - precipitation - Filtration - Disinfection," processes, Experimental research and practice show that conventional water treatment processes for the removal of endocrine disruptors have some effect, but the removal is limited, removal rate of organic matter is low; advanced treatment process effect on endocrine disruptors have a good removal. Currently, the most promising way of endocrine disruptors is photocatalytic oxidation degradation and biodegradation.

(3) Using of pesticides and fertilizers norms, strengthening industrial pollutant sources. Songliao basin As China's food base and China's agricultural. In severe pollution pesticides EDCs, the authorities should introduce relevant policies to restrict pesticide, fertilizer use, and strengthen non-point source pollution control measures in agricultural production due to vigorously promote ecological agriculture, to achieve pollution-free production; at the same time point source pollution should also strengthen the management and supervision of industrial production activities in wastewater brought stringent emissions standards requirements.

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