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Characteristics and Risk Assessment of Estrogenic Compounds in Rivers of Southern Jiangsu Province, China

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Abstract

Significant attentions are rising for estrogenic compounds in environment, because their potential impacts on water ecosystem and human health. Estrogenic compounds (Estrone[E1], 17b-Estradiol[E2], Estriol[E3], 17a-Ethinylestradiol[EE2] and Bisphenol A [BPA]) in rivers of southern Jiangsu, China were investigated to realize their distributions and risks. The results showed E1, E2, E3 and BPA ranged from 1.96 to 143.29ng/L in rivers, with the detection rates from 12.5% to 100%. These estrogenic compounds in waters showed higher contents in winter than in spring and autumn. Levels of E1, E2 and E3 were higher in rivers nearby livestock breeding areas, while the concentrations of BPA were higher in the rivers nearby industrial areas. The risk assessment of estrogenic compounds were performed by the calculation of risk quotient (RQ) based on the predicted no effect concentration (PNEC), which was deduced through a species sensitivity distribution (SSD) model. The RQ values of E1, E2, E3 and BPA were 0.02~1.87, 1.28~23.22, 0.01~0.80 and 0.03~0.44 respectively. These results imply that harmful ecological effects might happen in some rivers. It indicates that different anthropogenic activities will lead to diverse inputs of estrogen compounds into rivers and pose different risks.

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Keywords: estrogenic compounds; temporal and spatial distribution; risk assessment; river; southern Jiangsu

1. Introduction

Estrogenic compounds contain natural estrogens and synthetic estrogens which have estrogenic activities. The former widely exist in the vertebrate body, and the later are synthetic components, mainly from drugs,

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pesticide and surfactant[1, 2]. Estrogenic compounds in aquatic environment are acquiring prominent attention, because they are ubiquitous in the waters [3,4,5]. Many studies have shown that estrogenic compounds can damage human and animal reproduction, immune and nervous system, inducing deformity of reproductive organ, hermaphrodite or male feminization[6,7,8]. Therefore, the monitoring and assessment of estrogenic compounds in river has an important implication for protection of aquatic ecological system.

The rivers studied are situated in the southern Jiangsu province, one of economic-developed areas in China. Because of the densely population and the network rivers, pollutants from industry, agriculture and residential areas can enter the river environment through various pathways. Among these pollutants, estrogenic compounds are a group of ubiquitous pollutants. In addition, the rivers are main channels for estrogenic compounds entering a multipurpose lake-Taihu Lake. The purposes of this study are: 1. Investigate spatial distributions of estrogenic compounds in different rivers and link them with sources; 2. Research the variations of estrogenic compounds in different seasons; 3. Assess the ecological risks of rivers by the hazard quotient method.

2. Materials and Methods

2.1 Sample collecting

Surface water samples (0-0.5m) of rivers were collected according to the surroundings of sampling sites in October, 2012(fall), December 2012(winter) and May, 2013 (spring) (Fig.1). The sampling sites include four surrounding types (industrial area, residential area, farmland area, breeding area) according to the river locations. They comprise of six samples in industrial areas (S06, S07, S08, W08, Y07, Y08), six samples in

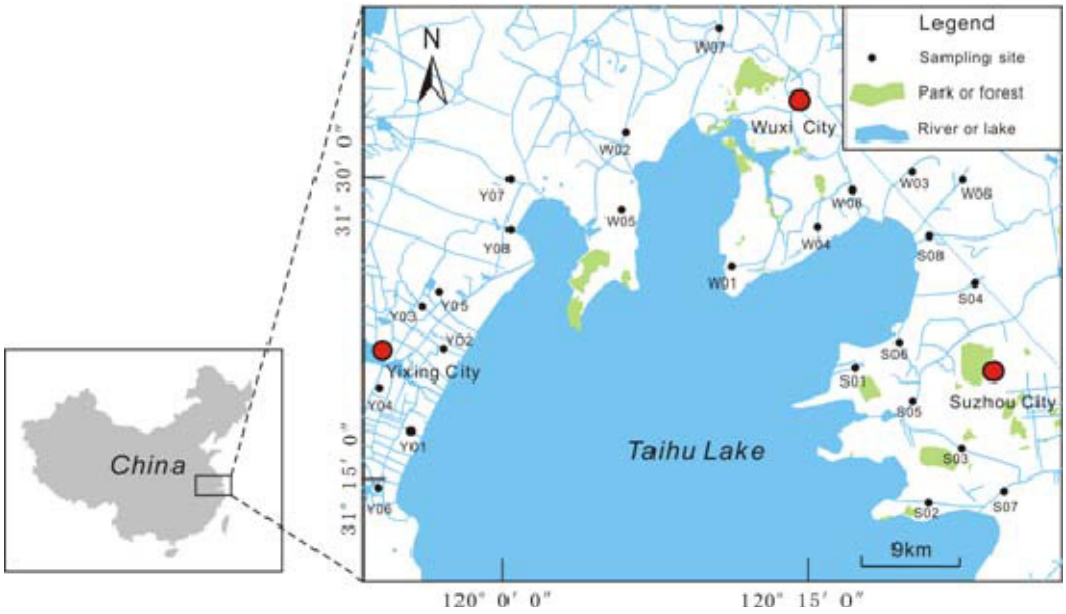

Fig. 1 Sampling map showing the locations in rivers of southern Jiangsu. These rivers are linked with Taihu Lake.

farmland areas (S01, W03, W04, Y01, Y02, Y03), five samples in breeding areas (S04、S05、W05、W06、Y06), and seven samples in residential areas (S02、S03、W01、W02、W07、Y04、Y05). Before sampling, the glass bottles were cleaned with distilled water, acetone, methanol, deionized water, and were cauterized

for 4-5 hours at 450 ^{o}C. All samples were conserved in 2L brown glass containers with 5‰ methanol, filtered through glass fiber membrane, and processed with SPE within 7 days.

2.2 Sample pretreatment

The samples (500ml) were filtered through filter membrane filtration of glass fiber (0.45μm pore size), and then concentrated by using four-channel automatic solid-phase extraction apparatus(Gilson, USA). The SPE HLB cartridges were eluted with 5 mL methanol and 5mL deionized water for twice, samples were passed through the cartridges at a flow rate of 5 mL/min in vacuum. After air dried for more than 30min, the detected compounds were eluted with 5×2 mL methanol. The extracts were dried in a multi-sample concentrator (Buchi Company, Switzerland), redissolved in 1 mL methanol. These sample vials were kept at -4^{o}Cfor later analysis.

2.3 Estrogenic compound analyses

Estrogenic standard compounds were supplied by Aldrich companies (USA). LC grade methanol was purchased from Merck Company (Germany). Distilled and deionized water were produced using a Milli-Q system. Liquid chromatography-mass spectrography (LC-MS, Agilent1290 Infinity，USA) was employed for identification and quantification of E1, E2, E3, EE2 and BPA.

The conditions of mass spectrometry were anion source (ESI) with focusing ion jet stream and multiple reactions monitoring. Specific parameters were as follows: the temperature of dry gas was 325^{o}C, the flow speed of dry gas was 6L/min at 35psi spray pressure, the temperature of sheath was 350^{o}C at 9L/min flow speed for sheath gas, capillary voltage was 4000V and jet nozzle voltage was 500V.

2.4 Quality control of sample analysis

In order to ensure the accuracy of the analysis, the blank sample, reagent blank sample and standard samples were appended in the experiment. The blank sample and the reagent blank sample didn't exhibit the target compounds. Recoveries of compounds ranged from 75.3% to 101.6% with less than10% of relative standard deviations. The detection limits of estrogenic compounds were calculated with three ratios of signal/noise (S/N). The limits of quantification for E1, E2, E3, EE2 and BPA in experiments were 0.09ng/L, 1.89ng/L, 1.06ng/L and 1.17ng/L, respectively.

2.5 Ecological risk assessment

The ecological risk assessment includes pollutant determination, ecological effect analysis and risk characterization. Pollutant determination is to recognize the temporal-spatial distribution of pollutants in rivers. Ecological effect analysis uses the toxicity data (no observed effect concentration, NOEC) of pollutants for dominant species in the representative area from EPA, and the screening principle is accuracy, appropriate and reliability [9,10]. The task of risk characterization is to integrate the relations of exposure and ecological effect, and give a value of ecological risk assessment.

The method of ecological risk assessment was used risk quotients in this paper.

$$RQ=PEC/PNECs \quad (1)$$

Where RQ is the hazard quotient, PEC is the environmental concentration (assumed to be the exposure concentration) of E1, E2, E3, EE2 and BPA, PNECs are the predicted no effect concentrations of E1, E2, E3, EE2 and BPA.

Using chronic toxicity data of estrogenic compounds fit species sensitivity distribution (SSD) to obtain the HC5 (HC5 express the pollutants concentration which can protect 95% of the species, and this concentration correspond 5% cumulative frequency in SSD)[11]. According to the evaluation factor method provided by TGD (technical guidance document on risk assessment) calculate PNECs of pollutants in water.

$$PNEC=HC5/AF \quad (2)$$

AF represents the assessment factor (1-5). The selecting value of AF should consider biological taxa of toxicology data, the quality and quantity of data, and fitting situation. Guidelines for interpreting RQ values indicate that the compounds pose a potential risk to ecosystems when RQ>1.0. However, considering the interaction of pollutants and the enrichment effect of aquatic organisms, RQ>0.3 is suitable for a potential risk to ecosystems in this area.

3. Results and discussions

3.1 Distribution of estrogenic compounds in river waters

Four estrogenic compounds (E1, E2, E3 and BPA) were detected in rivers of southern Jiangsu, except EE2 (Table 1). The median concentrations for four estrogenic compounds ranged from 2.96 to 143.29ng/L, with the detection frequency ranges of 12.5% to 100%, respectively.

Table 1 Characteristics of measured estrogenic compounds in rivers of southern Jiangsu

	E1(ng/L)	E2(ng/L)	E3(ng/L)	BPA(ng/L)
Concentration range	ND-11.23	ND-52.71	ND-47.85	48.24-725.94
Geometric mean	3.06	18.64	10.14	143.83
Median	2.96	17.20	18.37	143.29
Detection frequency (%)	20.8%	12.5%	19.4%	100%

ND is not detected

BPA was the detected compound in all samples, with values from 143.29ng/L to 725.94ng/L. BPA is a kind of important chemical intermediates, mainly used for raw materials of burning inhibitor, packaging plasticiser, household items and building coating [12]. Among sampling sites, the highest concentration of BPA was found at site Y07 within an industrial park, where the river received wastewater from enterprise (such as plastic, machinery and rubber factories).

Table 2 Maximum concentration of estrogenic compounds in rivers of different areas (ng/L)

River(Country)	E1	E2	E3	EE2	BPA	Reference
Jiulongjiang River (China)	321.02	74.4	39.8	ND	4687	[5]
Douro River(Portugal)	112.9	—	—	101.9	10700	[3]
River in Tianjing(China)	49.8	21.2	46.4	35.6	—	[16]
Liobregat River(Spain)	2.8	ND	ND	ND	—	[17]
Five rivers in South East Queensland（USA）	20.91	3.7	—	0.52	52	[18]
Three rivers in south Rio de Janeiro(Brazil)	ND	ND	7.27	ND	—	[19]
Some rivers (Brazilian)	39	7.3	2.3	25	84	[20]
Rivers in southern Jiangsu	11.23	52.71	47.85	—	725.94	This study

ND is not detected

Among the three natural estrogens, was the detected ratios of E1, E2 and E3 were 20.8%, 12.5% and 19.4% respectively. Studies have pointed out that 95% of E2 will converted into E1 within 1~3 hours in sewage sludge[5,13]. And researchers also found that the detection rate of E1 was higher than E2 due to the conversion of E2 to E1[14,15]. In this study, the highest concentrations of E1 (11.23ng/L) and E3 (47.8ng/L)

occurred in the river waters near the urban residential area (W07 and S03), and the highest concentrations of E2 (52.71ng/L) occurred in the river near a livestock breeding area. It is indicated that natural estrogens are mainly produced from excretion of human and animal [2].

Comparisons of estrogenic compounds in rivers of southern Jiangsu and other areas were shown in table 2. In most studies, the concentrations of E3 and E1 were higher than E2. The concentrations of estrogenic compounds in rivers of southern Jiangsu were similar to domestic urban rivers, but significantly higher than rivers from other countries.

Distributions of estrogenic compounds in rivers situated in different functional areas were shown in Fig.2. It was shown that BPAs followed the order of industrial area>residential area> breeding area>farmland area. Because BPA was mainly for raw material of industrial products, the concentrations of BPA were higher in the industrial and residential areas. The concentrations of E1, E2 and E3 were higher at residential area and breeding area than industrial area and farmland area. Those estrogens can enter the water environment through human excretion and animal fodder, increasing concentrations in these rivers [21].

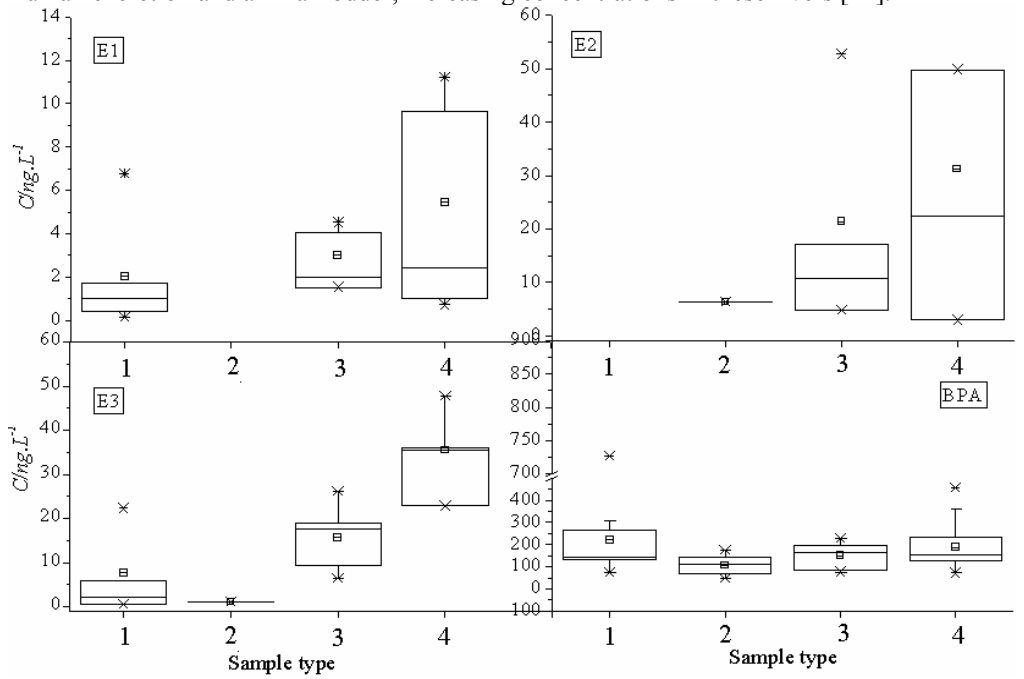

Fig. 2 Distributions of estrogenic compounds in river waters of different areas
1-industrial areas；2-farmland areas；3-breeding areas；4-residential areas

3.2 Seasonal distribution of estrogenic compounds

Estrogenic compounds in different seasons were shown in Fig.3. Concentrations of BPA in rivers showed winter>spring>autumn (mean 196.48 ng/L, 167.87ng/L, 90.21ng/L respectively, $P<0.001$). Winter is the least rainfall reason and inducing less dilution of BPA than spring and autumn.

The concentrations of E1, E2 and E3 in rivers changed in three seasons. The concentrations of E1, E2 in winter were higher than those in spring and autumn, except E3. The probably reason was that plentiful rainfall could dilute the concentration of E1 and E2 in spring and autumn. E3 was not detected in autumn. And the variations of E3 were not observed in spring and winter ($P=0.828$). But the detection rate of spring samples (41.67%) was higher than winter samples (8.33%). The possible interpretation was E3 occurred as an intermediate of E1 and E2, which transformed more quickly in higher temperature [22].

3.3 Risk analysis of estrogenic compounds

According to the method of ecological risk assessment above, NOECs of E1, E2, E3 and BPA were obtained as chronic toxicity data from ECOTOX database. The toxicity and exposure data for estrogenic compounds have been log-transformed to satisfy the log-normal distribution. The values of HC5 for E2 and BPA were 6.82 ng/L and 4.91μg/L by fitting curves of species sensitivity distribution. Based the calculation formula of PNEC = HC5/AF (AF=3 according to biological category, quality, quantity and data fitting in this area). PNECS for E2 and BPA were 2.27ng/L and 1.64μg/L. Because the toxicity data for E1 and E3 cannot build species sensitivity distribution, PNECS for E1 and E3 were 6ng/L, 60μg/L based on the previous research [9]. Exposure Assessment will adopt the measured concentration instead of predicted environmental concentration (PEC). The RQ_S were calculated by $PNEC_S$ and PEC_S, as shown in Fig.4.

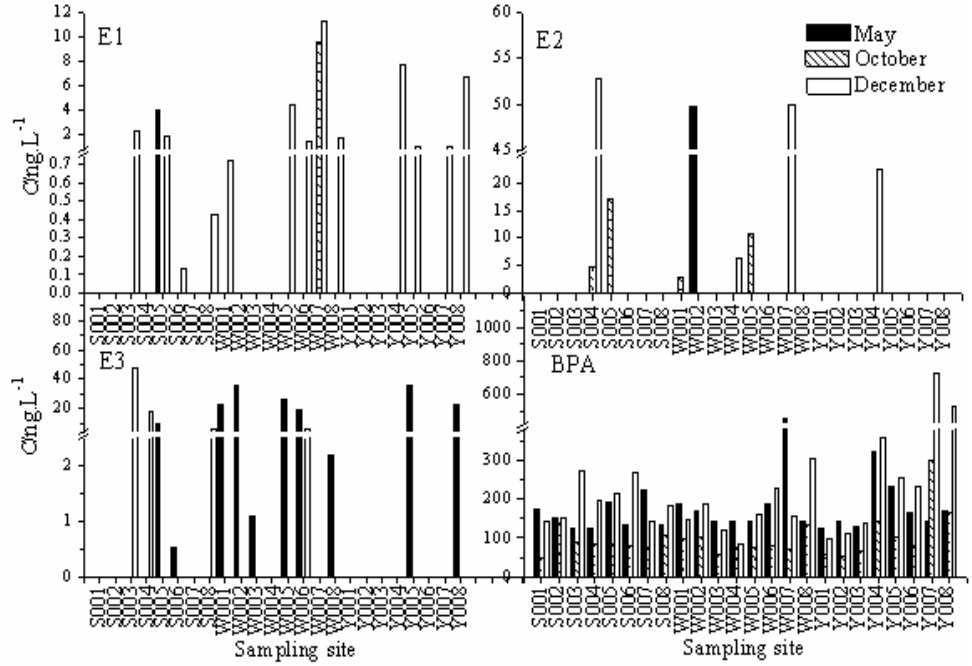

Fig.3. Seasonal distributions of estrogenic compounds in rivers

The RQs of BPA ranged from 0.03 to 0.44. And the sampling sites for the RQ_S greater than 0.3 accounted for 2.78%, which was not significant risk in this study area. But on the basis of community regulations, the total concentrations of phenols must be lower than 500ng/L in drinking water, but phenolic compound must be no higher than 100ng/L [23,24]. Taihu lake can be a drinking-water source for surrounding cities. Based on the fact that most of winter samples had exceeded 100ng/L, the ecological risk of BPA should be considered in the western rivers.

For estrogenic compounds detected, RQs of E1, E2 and E3 ranged from 0.02 to 1.87ng/L, 1.28 to 23.22 ng/L, and 0.01 to 0.08ng/L, respectively. The risk probabilities of E1, E2 and E were 53.3%, 100% and 57.14% respectively with RQs exceeding 0.3. Therefore, E1, E2 and E3 can caused the potential ecological risk, especially considering a composite interaction.

4. Conclusion

Estrogenic compounds (E1, E2, E3 and BPA) can be detected significantly in rivers of southern Jiangsu, except EE2. Estrogenic compounds present a uneven distribution in space, according to the locations. Levels of E1, E2 and E3 are higher in the rivers nearby livestock breeding areas, but BPAs show higher concentrations nearby industrial areas. The seasonal changes show that estrogenic compounds in winter are higher than in spring and autumn. These results indicate that different anthropogenic activities and hydrological regimes will lead to differences in distributions of estrogenic compounds. RQ_S of estrogenic compounds may exceed threshold sometime, so harmful ecological effects might happen in this area, further investigation and risk mitigation actions for estrogenic compounds are needed.

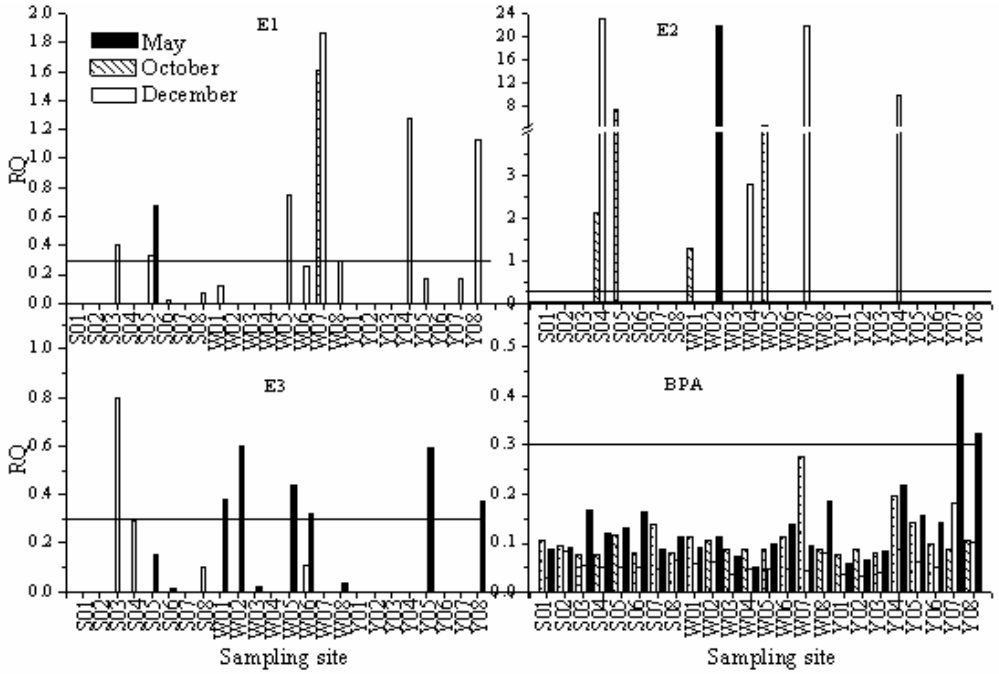

Fig. 4. Risk Quotient values of estrogenic compounds in surface waters

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