Supersaturation

P 3.5 mmol/L   P 6.0 mmol/L   P 9.0 mmol/L

Aggregate size, fractal dimension

**Phosphorus recovery from wastewater
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Distribution and seasonal variation of estrogenic endocrine disrupting compounds, N-nitrosodimethylamine, and N-nitrosodimethylamine formation potential in the Huangpu River, China

Ai Zhang, Yongmei Li*, Ling Chen

State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China. E-mail: za19891207@163.com

A B S T R A C T

Detection of estrogenic endocrine disrupting compounds (EDCs) and N-nitrosodimethylamine (NDMA) in drinking water has led to rising concerns. There are, however, a paucity of studies on the distribution and seasonal variation of NDMA and NDMA formation potential (NDMA-FP) in natural waters, especially in China. For EDCs, limited studies have investigated the distribution and seasonal variation of estrone (E1), 17β-estradiol (E2), estriol (E3), 17α-ethinylestradiol (EE2), technical-nonylphenols (t-NP), and bisphenol A (BPA) in Shanghai. In this study, water samples were collected from 11 sampling sites along the Huangpu River in 2012. The distribution and seasonal variation of EDCs, NDMA, and NDMA-FP were investigated. The results showed that all of the 11 sampling sites were contaminated by the target compounds. Compared with E2 and EE2, higher E1 and E3 concentrations were usually detected in the Huangpu River. The values of 17β-estradiol equivalents (EEQ) suggest a high possibility of endocrine effects on exposed organisms in the Huangpu River. NDMA-FP and t-NP were the dominant contaminants among the eight target compounds. The detection rates of the target compounds and their concentrations were both higher in dry seasons than in wet seasons. Higher concentrations of target compounds were observed in urban sampling sites near drainage outlets, and also in suburban sampling sites where intensive livestock farming and farmlands were located.

Introduction

The continuous growth in human population has created a corresponding increase in the demand for the Earth's limited supply of fresh water. One of the most common relevant topics in the environmental field nowadays is water quality. Recent decades have brought increasing concern for the potential adverse human and ecological health effects resulting from the production, use, and disposal of numerous chemicals that offer improvements in industry, agriculture, medical treatment, and even common

household conveniences. Among these chemicals, global concern about the presence of estrogenic endocrine disrupting compounds (EDCs) and N-nitrosodimethylamine (NDMA) has attracted particular attention (Schreiber and Mitch, 2006; Chen et al., 2007).

Among EDCs, the presence of steroid estrogens (such as estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethinylestradiol (EE2)) and phenolic xenoestrogens (such as technical-nonylphenols (t-NP) and bisphenol A (BPA)) deserves particular attention, because the former possess the highest estrogenicity and the latter have moderate estrogenic potency and widespread applications (Vethaak et al., 2005). Their adverse effects on the reproductive functions of aquatic species (e.g., feminization of male

fish, snail, and tadpoles, and induction of vitellogenin for male fish and turtles) and influence on humans (e.g., inducing prostate cancer, reproductive tract disorders, low sperm counts, and breast cancer) have been observed worldwide (Patrolecco et al., 2006). Therefore, a comprehensive investigation of the environmental exposure level of EDCs has become a pressing issue. NDMA is a highly water soluble nitrosamine that is a member of a family of extremely potent carcinogens and mutagens known as N-nitrosamines. Their cancer potencies are much higher than those of the trihalomethanes. NDMA was used as an intermediate in the production of rocket fuel, an additive to lubricants, and a solvent in the fiber and plastic industry, leather tanning, metal casting, and food processing. In recent decades, NDMA was also found to be a novel disinfection byproduct from chloramination or chlorination. The NDMA formation potential (NDMA-FP) has been used to characterize NDMA precursors. NDMA and NDMA-FP have been discovered in various surface and ground waters and have been linked to ecological impacts at trace concentrations (Charrois et al., 2004; Van Huy et al., 2011). NDMA persistence within surface waters is a major concern for drinking water utilities. To further evaluate the potential threats of these chemicals in aquatic ecosystems, one must examine their distribution, transport, transformation, and fate.

In the past decades, some publications have been devoted to the occurrence of EDCs, NDMA, and NDMA-FP in natural waters. Reports on their levels in natural waters are summarized in **Table 1**. EDCs and NDMA were also discovered most frequently in water bodies in China (Lei et al., 2009; Lu et al., 2010). In the majority of studies for target compounds in natural waters of China, the levels were generally higher in comparison with those found in the USA, Austria, South Korea, and European countries. An additional problem is the absence of water quality threshold standards with regard to estrogenic activity and NDMA in drinking water and wastewater treatment plant effluent water in China. Hence, the impacts to humans of the EDCs, NDMA, and NDMA-FP in natural waters should not be ignored in China. However, there is a paucity of studies on the distribution and seasonal variation of NDMA and NDMA-FP in natural waters, especially in China. It is necessary to monitor their levels in natural waters so as to evaluate the risks to humans and to provide useful information for drinking water and wastewater treatment.

Shanghai is one of the most developed and urbanized cities in China, with a population of more than 23 million. It is also the largest industrial base and foreign trade port along the estuary coastline of the Yangtze River in central China. The huge population and the highly developed industry of Shanghai have led to an extensive

Table 1 Concentrations of EDCs, NDMA and NDMA-FP in natural waters presented in the literature (unit: ng/L)

Locations	E1	E2	E3	EE2	NP	BPA	References
Jalle d'Eysines River, France	ND–30	ND–1.5	ND–1.8	ND–2	NA	NA	Labadie and Budzinski, 2005
Dutch surface water, Netherlands	0.3–7.2	0.8–1.0	NA	0.3–0.4	110–4100	8.8–1000	Vethaak et al., 2005
Scheldt estuary, Belgium	0.37–10	ND	NA	ND	NA	NA	Noppe et al., 2007
Rhine, Ahr, Agger River, Germany	1.3–9.2	NA	NA	0.3-1.0	NA	NA	Hintemann et al., 2006
The area of Thessaloniki, Greece	ND	ND	ND	ND	152–338	15–138	Arditsoglou and Voutsa, 2010
Mondego River estuary, Portugal	ND	ND	ND	ND	NA	ND–589.5	Ribeiro et al., 2009
19 Water utilities in USA	ND–0.9	ND–17	NA	ND–1.4	ND–130	ND–14	Benotti et al., 2009
414 Samples spread across Austria	ND–4.6	ND–1.2	ND–1.9	ND–0.33	ND–890	ND–600	Hohenblum et al., 2004
Dan-Shui River, Taiwan, China	22–66.2	1.4–33.9	12–73.6	7.5–27.4	NA	NA	Chen et al., 2007
Dagu River, China	5.0–55.3	0.9–33.4	2.3–46.4	ND–35.6	NA	NA	Lei et al., 2009
Urban riverine water of Guangzhou	ND–65	ND–2	ND–1	ND–1	36–33231	6–881	Chen et al. 2008
Lake Taihu, China	ND–15.8	ND–10.8	NA	ND–16.4	262.4–1442.7	9.15–34.42	Lu et al., 2011
The Yangtze River, Nanjing, China	0.8–1.25	0.8–0.97	5.79	NA	344.4–536.6	34.55–60.69	Lu et al. 2010
The Pearl River Delta, South China	1.5–11.5	NA	NA	NA	276–2457	8.4–628	Peng et al., 2008
Yangtze River, China	0.9–2.98	0.26–1.8	ND–4.37	ND–2.67	100.2–288.8	65.0–710.6	Jiang et al., 2012
The Pearl Rivers, China	ND–75.0	ND–7.5	NA	NA	28.1–8890	2.2–1030	Zhao et al., 2009

Locations	NDMA	NDMA-FP	References
Japan	ND–4.3	NA	Asami et al., 2009
Tokyo, Japan	< 0.5–3.4	11–185	Van Huy et al., 2011
Municipal wastewater effluents, USA	7.6–400	247–1310	Schreiber and Mitch, 2006
Buyukcekmece watershed, Turkey	NA	< 2–1648	Aydin et al., 2012
Alberta, Canada	2–180	NA	Charrois et al., 2004
Inlets of 12 DWTPs in Beijing, China	ND–13.9	NA	Wang et al., 2011
Jialu River, China	31.7 ± 49.5	NA	Ma et al., 2012

NA: not available; ND: not detected.

usage of chemicals including EDCs, NDMA, and NDMA-FP. The Huangpu River is the largest river in Shanghai, and is the most important shipping artery and the major drinking water source of the city, providing most of the raw water (6.3 million tons/day). By the end of 2010, 2313 million m^3 of wastewater was produced each day in Shanghai. However, the wastewater treatment rate was only 69% in the suburban area and 88% in the urban area. About 419 million m^3 of untreated raw wastewater was discharged directly into the Huangpu River (Shanghai Water Authority, 2013). The extensive usage of water and large discharge of wastewater indicate great release of EDCs, NDMA, and NDMA-FP into the Huangpu River.

However, little information is available for NDMA and NDMA-FP concentration levels in Shanghai. Although occurrence of EDCs in China has been investigated, the results are inconsistent and limited studies have investigated the distribution and seasonal variation of E1, E2, E3, EE2, t-NP, and BPA in Shanghai. Therefore, this work focused on the distribution and seasonal variation of EDCs, NDMA, and NDMA-FP in the surface water of the Huangpu River by conducting sampling events in 2012. Eleven sampling sites were selected along the Huangpu River and 8 target chemicals (including E1, E2, EE2, E3, NP, BPA, NDMA, and NDMA-FP) were analyzed. The results will provide important background data for risk assessment and contamination control of EDCs and NDMA in the aquatic environment of this area.

1 Materials and methods

1.1 System description and sampling site selection

The total length of the Huangpu River is 114 km, with a basin area of 24000 km^2 (Shanghai Water Authority, 2013). It originates from Dianshan Lake. It travels northeast and finally enters into the Yangtze Estuary (**Fig. 1**).
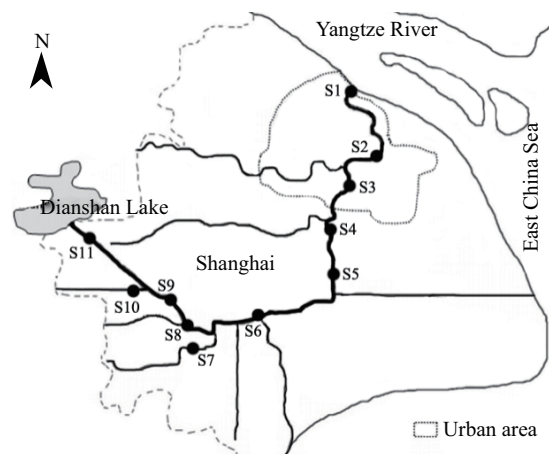
Fig. 1   Location of the eleven sampling sites of the Huangpu River.

The upper reaches of the Huangpu River flow through the suburbs of Shanghai, characterized by intensive agricultural activities, especially animal breeding operations. Its lower reaches flow through the urban area, with intensive industrial and residential activities. The water quality of the Huangpu River is impacted by a variety of sources, including point sources such as municipal wastewater treatment plant effluents, and non-point sources such as storm-water runoff and waste from confined animal feeding operations applied to farm fields.

The selection of sampling sites primarily focused on areas considered susceptible to contamination from human, industrial, and agricultural wastewaters. Eleven sampling sites were selected along the Huangpu River, representing a wide range of geography and hydrogeology. Specific information on the individual sampling site is provided in **Table 2**.

1.2 Sample collection

Samplings were conducted in February, April, June, October, and December 2012. Two sampling events were

Table 2	Descriptions of the sampling sites	
Site	Location	Description
S1	31°22′55′′N, 121°30′11′′E	Lower reach of the Huangpu River
S2	31°15′11′′N, 121°32′01′′E	Lower reach of the Huangpu River
S3	31°12′49′′N, 121°30′16′′E	Middle reach of the Huangpu River
S4	31°08′29′′N, 121°27′18′′E	Middle reach of the Huangpu River
S5	31°02′50′′N, 121°28′40′′E	Middle reach of the Huangpu River
S6	30°58′03′′N, 121°17′57′′E	Upper reach of the Huangpu River. It is the largest drinking water source of Shanghai, supplying about 5.5 million ton raw water per day
S7	30°55′12′′N, 121°11′31′′E	Damao river. It accounts for 30% of the water of the Huangpu River
S8	30°57′41′′N, 121°09′31′′E	Yuanxiejing river. It accounts for 30% of the water of the Huangpu River
S9	30°58′37′′N, 121°09′00′′E	Xietang river. It accounts for 40% of the water of the Huangpu River, and supplies 420,000 ton raw water per day for surrounding regions
S10	31°01′31′′N, 121°02′38′′E	Taipu river. It originates from Tai Lake, and supplies about 260,000 ton raw water per day for surrounding regions
S11	31°05′04′′N, 120°59′30′′E	Outlet of Dianshan Lake

carried out in the middle and the end of each sampling month. The convenience and safety of sample collection were considered in selecting sampling points. All samples were collected from the center of the stream (1 m deep below the water surface) using consistent protocols and procedures. Water samples for chemical analysis were stored in pre-cleaned silanized amber glass bottles. Immediately after sampling, an appropriate amount of ascorbic acid (1 g/L in the water sample) was added to the sample to suppress possible biotic activities. Then samples were immediately chilled and sent to the laboratory. To minimize the possible contamination of samples, throughout sample collection and processing, EDCs, NDMA, and NDMA-FP were restricted. Samples were stored at 4°C prior to treatment and were treated and analyzed within 48 hr.

1.3 Chemicals

E1, E2, E3, and EE2 were purchased from Sigma-Aldrich (St. Louis, USA). BPA and t-NP (technical grade) were obtained from Aldrich (Milwaukee, WI, USA). NDMA was obtained from Chem Service Inc. (West Chester, PA, USA). The above chemicals were used as standards for establishing analytical methods. The purity of all the standards was greater than 98%. Standard solutions of 1 g/L were prepared in methanol and stored at 4°C. NDMA-d_6 was purchased from Chem Service Inc. (West Chester, PA, USA) and was used as an isotope-labeled surrogate standard. All organic solvents, including methanol, acetonitrile, acetone, hexane, and dichloromethane purchased from Sigma-Aldrich, were of high-performance liquid chromatography (HPLC) grade. The water employed was purified by a Milli-Q system, with a resistivity higher than 18.2 MΩ cm at 25°C. Sodium hypochlorite and ammonium chloride bought from Alfa Aesar (Ward Hill, MA, USA) were used to prepare monochloramine. Other regents used in this study were of analytical grade and supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

1.4 Sample preparation and analytical methods

Water samples were filtered through 0.7 μm, pre-baked glass fiber filters to remove insoluble materials and extracted using the solid-phase extraction (SPE) method.

For analysis of E1, E2, EE2, and E3, 1 L of water sample was extracted with C18 SPE according to Zeng et al. (2009). The extract was evaporated to dryness under a nitrogen stream and was reconstituted to 0.5 mL with methanol. A procedural blank using purified water was also run alongside the samples as an assay control. An Agilent 1100 HPLC (USA) equipped with a reversed-phase C-18 column (4.6 mm × 250 mm, 5 μm, Agilent, USA) was used to analyze samples. The injection volume was 50 μL and the flow rate was 1 mL/min. The separation was performed under gradient elution conditions using acetonitrile and water. The solvent program used for E2, EE2, and E3 was as follows: initial conditions 70% of

water linearly reduced to 30% over 12 min, then linearly decreased to 0% over 0.3 min, and then kept isocratic for 10 min. An excitation wavelength of 228 nm and emission wavelength of 316 nm were used for fluorescence detection of E2, EE2, and E3. For E1, a wavelength of 200 nm was used for UV detection at a temperature of 40°C. The solvent program used for E1 was kept at initial conditions of 50% of water for 15 min.

For BPA and t-NP analysis, SPE was used to extract BPA and t-NP in water samples. The Supelclean TM LC-18 cartridges (500 mg, 3 mL) were obtained from Supelco (USA). The extraction procedure was derived from the method described by Zhao et al. (2008). The extract was evaporated to dryness under a nitrogen stream and was reconstituted to 0.5 mL with methanol. A procedural blank using purified water was also run alongside the samples as an assay control. BPA in the extracts was determined by an Agilent 1100 HPLC (USA) equipped with a fluorescent detector and a reversed-phase C-18 column (4.6 mm × 250 mm, 5 μm, Agilent, USA). For BPA, the mobile phase was acetonitrile/water (50:50, V/V). The excitation and emission wavelengths were 230 and 290 nm, respectively. For t-NP, the mobile phase was acetonitrile/water (80:20, V/V) and the detection wavelengths were 225 nm for excitation wavelength and 300 nm for emission wavelength. The process was stopped after 25 min. The flow rate was 1 mL/min. The injection volume was 20 μL.

For the analysis of NDMA, samples of 500 mL were used for SPE using procedures described by the US EPA Method 521. NDMA was determined using Ultra Performance Liquid Chromatography/Electrospray Ionization tandem Mass Spectrometry (UPLC-ESI-MS, ESI source, TAQ Quantum, Thermo Fisher Scientific Inc., USA) with an Eclipse XDB C18 column (150 × 2.1 mm, 3.5 μm; Agilent). The mobile phase was composed of solvent A (2 mmol/L of ammonium acetate) and solvent B (100% methanol). The solvent gradient program consisted of solvent B increasing from 10% to 45% in 4 min, then up to 100% in 1 min and kept for 5 min, and finally returning back to 10% in 1 min, followed by a 2 min re-equilibration prior to the sample injection. The flow rate was 150 μL/min, and the sample injection volume was 10 μL. Positive electrospray ionization combined with the multiple reaction monitoring mode was used. The optimal ionspray parameters were as follows: curtain gas (N_2) at 8, ion source gas at 45, and ionspray voltage at 4500 V. The multiple reaction monitoring transitions were m/z 75–43 (quantification) and m/z 75–58 (confirmation) for NDMA, and m/z 81–46 for NDMA-d_6.

To quantify the NDMA-FP, water samples of 500 mL were exposed to monochloramine with the concentration of initial chlorine at 4 mmol/L (initial Cl(I) concentration 4 mmol/L) for an extended period (10 days). Monochloramine was prepared according to the method described by Le Roux et al. (2011). The concentration of NDMA

formed serves as a surrogate for all the compounds that can be converted into NDMA during chloramination. Samples (500 mL) were buffered at pH 6.9 ± 0.4 with 10 mmol/L phosphate buffer and then reacted with monochloramine (initial Cl(I) concentration 4 mmol/L). The reaction containers were stored and protected from light at 23 ± 2°C. The reaction was halted after 10 days by the addition of 1.1 mmol/L of ascorbic acid. Then the concentrations of NDMA of the samples were analyzed as described above.

1.5 Quality control and quality assurance

Standard solutions were prepared at 6 levels by using appropriate volumes of the working standard solution. For EDCs, analytes were quantified by the external standard quantification procedure. The standard curves of peak area versus injected amount were obtained by measuring the resulting peak area at a given injected amount. The solid phase extraction-high performance liquid chromatography-fluorescence detection method (SPE-HPLC/FLD) was employed in the analysis of EDCs, due to their wide linear ranges (5–1500 ng/L) and good correlation coefficients ($R^2 > 0.992$). For NDMA and NDMA-FP, 25 ng of NDMA-d_6 was added to 500 mL samples. The concentration of NDMA was obtained using NDMA-d_6 as an internal standard. The solid phase extraction-ultra-performance liquid chromatography-electrospray ionization mass spectrometry method (SPE-UPLC/ESI/MS) was employed in the NDMA and NDMA-FP analysis, due to their wide linear ranges (5–1500 ng/L) and good correlation coefficients ($R^2 > 0.994$). The limits of detection (LODs) and the limits of quantification (LOQs) of target compounds in surface water ranged from 2.0 to 3.1 ng/L and 6.0 to 10.3 ng/L (**Table 3**), respectively. The recoveries of the target compounds (100 ng/L) spiked to filtered surface water samples were higher than 80% for EDCs, and 77%–87% for NDMA ($n = 5$). All samples were analyzed in duplicate, and the relative standard deviations ($n = 2$) were less than 10%. Laboratory blanks were used to assess potential sample contamination. Analysis of reagent blanks demonstrated that the analytical system and glassware were free of contamination. Blank contamination was not subtracted from environmental results.

Table 3 Recoveries of solid-phase extraction, limits of detection (LOD) and limits of quantification (LOQ) of the target compounds

Compound	Recovery ± SD (%)	LOD (ng/L)	LOQ (ng/L)
E1	89 ± 3	2.4	8.8
E2	96 ± 5	2.1	7.2
EE2	86 ± 6	2.3	8.0
E3	88 ± 5	2.6	7.5
NP	85 ± 3	3.1	10.3
BPA	94 ± 5	2.0	6.0
NDMA	82 ± 5	3.0	9.0

1.6 Calculation of EEQ

The endocrine activity of environmental samples is usually assessed by specific bioassays. However, an evaluation of the endocrine activity from chemical analyses could be made according to the following equations:

$$EEQ = EEF_i \times C_i$$

where, EEQ_i is the estradiol equivalent of the compound i in the sample, C_i is the measured environmental concentration and EEF_i is the endocrine equivalent of the compound i. Each individual estrogen concentration was multiplied by its relative potency to gain the EEQ_i. The sum of the EEQ_i was expressed as EEQ. The calculations were based on the hypothesis that the effect of each estrogen was additive, as has been shown in some other studies (Sun et al., 2009). Based on the median effective dose values, the EEFs of the target EDCs to E2 follow the orders of EE2 (1.25) > E2 (1.00) > E1 (0.33) > E3 (2.40 × 10^{-2}) > NP (1.36 × 10^{-3}) > BPA (1.65 × 10^{-4}) (Lei et al., 2009).

2 Results and discussion

2.1 Overall concentration levels and detection rates of target compounds

EDCs, NDMA, and NDMA-FP were detected at all 11 sampling sites. The concentrations of the target compounds in water samples of the eleven sites from February to December in 2012 are summarized in **Fig. S1** and **Table 4**. The mean value of the two sampling events in each month was shown as the data of that month. As shown in **Fig. S1**, the selected compounds were all in ng/L level except for t-NP. t-NP was the most abundant EDC recorded and its concentration ranged from 20.24 to 1389 ng/L (mean 259.5 ng/L). The concentration levels of other EDCs in all samples were ND–94.14 ng/L for E3 (mean 40.79 ng/L), ND–74.79 ng/L for E2 (mean 13.57 ng/L), ND–55.37 ng/L for EE2 (mean 11.99 ng/L), < LOQ–687.5 ng/L for BPA (mean 95.22 ng/L), ND–93.45 ng/L for E1 (mean 30.42 ng/L), < LOQ–58.78 ng/L for NDMA (mean 29.47 ng/L), and 43.40–331.4 ng/L for NDMA–FP (mean 131.1 ng/L).

As shown in **Table 4** and **Fig. S1**, BPA, t-NP, NDMA, and NDMA-FP were all detected at each sampling site in each sampling event, while E1, E2, EE2, and E3 were not always detected at each site. Among the four estrogens, E1 was the most frequently detected compound in all the 11 samples in February, June, October, and December, while in April, E1 was not detected at S11. E3 also showed a high detection frequency with detection rate of 100% in February, April, and December, while it was not detected at S2 in June and at S9 and S10 in October. E2 was found

Table 4	Concentrations and frequencies of target compounds detected in water samples										
			E3	E2	EE2	t-NP	BPA	E1	NDMA	NDMA-FP
February, 2012	Detection rate (%)		100	45	73	100	100	100	100	100
	Concentration (ng/L)	Med	47.24	ND	< LOQ	160.8	81.12	10.93	27.96	184.8
		Max	79.33	12.78	22.00	245.1	190.1	17.17	45.98	331.4
		Min	25.40	ND	ND	72.76	21.03	10.31	15.05	116.8
April, 2012	Detection rate (%)		100	9	100	100	100	91	100	100
	Concentration (ng/L)	Med	24.54	ND	31.97	60.58	37.65	40.32	47.27	140.8
		Max	46.53	16.97	55.37	113.6	188.7	93.27	58.78	187.0
		Min	9.510	ND	13.81	20.24	8.900	ND	< LOQ	91.34
June, 2012	Detection rate (%)		91	18	9	100	100	100	100	100
	Concentration (ng/L)	Med	40.38	ND	ND	56.06	20.39	10.41	14.09	87.62
		Max	89.85	35.08	< LOQ	125.6	52.06	17.44	51.38	100.8
		Min	ND	ND	ND	43.66	< LOQ	9.090	9.160	43.40
October, 2012	Detection rate (%)		82	100	0	100	100	100	100	100
	Concentration (ng/L)	Med	12.78	18.79	ND	359.6	28.34	18.02	24.70	103.1
		Max	24.09	38.45	ND	472.3	76.39	93.45	37.27	130.5
		Min	ND	7.690	ND	207.0	6.160	< LOQ	16.21	61.89
December, 2012	Detection rate (%)		100	100	100	100	100	100	100	100
	Concentration (ng/L)	Med	60.56	35.71	20.48	667.4	100.8	56.64	34.50	137.3
		Max	94.14	74.79	29.73	1389	687.5	89.03	44.65	235.7
		Min	50.47	16.25	12.52	200.0	58.56	11.88	15.68	103.3

in all the samples in October and December, while in February, June, and April, the detection rates were below 50%, with the median concentrations all calculated as ND. EE2 was the least frequently detected compound.

Compared with the data presented in the literature (**Table 1**), the concentration levels and detection rates of E1, E2, EE2, and E3 were higher than those shown in previous studies in other countries, but were at the same levels as observed in China. The high concentrations and detection rates of E1, E2, EE2, and E3 in this study might reflect the relatively wide use and discharge of estrogens into the Huangpu River. This could be partially attributed to the family planning policy of birth control in China, where the usage of EE2-based oral contraception pills is more prevalent than in any other country (Zhou et al., 2010). China is a country with the highest consumption of contraceptive pills, which can explain the high concentrations of E1, E2, E3, and EE2 in water bodies.

The results also indicated that the concentrations of E1 were higher than those of E2. It had been reported that concentrations of E1 were higher than those of E2 in river water because of the oxidation of E2 to E1 (Charrois et al., 2004). Lei et al. (2009) also reported that E2 can easily transform into E1 by oxidation in the aquatic environment. Therefore, greater amounts of E1 compared with E2 would be expected in surface water.

Higher concentrations of E3 than those of E2 and EE2 were also found in the Huangpu River. A possible explanation is that E2 and EE2 can be transformed easily into E1 and then further degraded into E3 in the aquatic environment. Xu et al. (2012) reported that daily urine

excretions of E1, E2, and E3 in Asian premenopausal women were 2.66, 1.09, and 5.68 μg; in menstruating females, 8, 3.5, and 4.8 μg; in menopausal women, 4, 2.3, and 1 μg; and in pregnant women, 600, 259 and 6000 μg, respectively. In all of these excretions, the levels of E1 and E3 were higher than those of E2. These would also explain the higher levels of E1 and E3 in the Huangpu River.

Compared with data in the literature shown in **Table 1**, the concentrations and detection rates of t-NP and BPA in this study were higher than those reported in surface water in European countries and USA, but were close to those reported in China. The nonylphenols were found in various Chinese rivers at concentrations of up to 97.6 ng/L (Yu et al., 2009). The detected BPA levels in various Chinese rivers are up to 1030 ng/L as shown in **Table 1**. This could be partially attributed to the relatively large use of t-NP and BPA in China. For example, in the USA, NPs and nonyphenols have been removed from laundry detergents (McCoy, 2007). Nevertheless, these compounds have not been effectively restricted in China. For the Huangpu River, it receives not only treated wastewater, but also untreated domestic sewage, industrial wastewater, and livestock and poultry wastewater from the catchment with its high population density. This can also explain the high concentrations of EDCs in the Huangpu River.

Concentrations of NDMA in this study were consistent with those reported in other investigations on surface water in China (**Table 1**); but they were higher than those detected in five rivers in Tokyo (< 0.5–3.4 ng/L). This indicates relatively high pollution from nitrosamines in China. As NDMA is a disinfection byproduct from chloramination or

chlorination of wastewater in the presence of ammonia, the general use of chloramination and chlorination in facilities may explain the higher levels of NDMA in surface water in China. Moreover, contamination of surface water by treated or raw wastewater will also increase the concentration of nitrogenous organic matter, which may act as NDMA precursors, thus increasing the concentration of NDMA-FP.

The concentrations of NDMA-FP in our investigation were in the range of 43.40–331.4 ng/L. This is higher than the levels detected in surface water in Tokyo, but lower than the municipal wastewater effluents in the USA as shown in **Table 1**. Although the formation mechanisms and precursors of NDMA are still not well understood, research evaluating the NDMA formation potential of several compounds has reported that a dissolved organic nitrogen precursor is required for NDMA formation (Selbes et al., 2013). Since NDMA-FP is unavailable for other investigations in China, the present data may imply a relatively high contamination by dissolved organic nitrogenous compounds in the Huangpu River.

2.2 Estimation of endocrine activity in the Huangpu River

EEQ in each month of each sampling site and average EEQ of five months of 11 sampling sites were calculated using the data shown in **Table S1**. As presented in **Fig. 2**, the EEQ value ranged from 3.310 to 127.6 ng/L. These values suggest a high possibility of endocrine effects on the exposed organisms in the Huangpu River. Since the EEQ values in the present study were calculated using only six EDCs (E1, E2, EE2, E3, BPA, and t-NP), the actual EEQ values in water samples of the Huangpu River are expected to be higher due to the possible presence of other estrogenic compounds, although the occurrence of anti-estrogenic compounds is also possible. Estrogenic contamination in the aquatic environment is a global phenomenon, especially in Asian countries (Duong et al., 2010). In other Asian countries, the estimated estrogenic activity in river water ranged from values below detection limits to 66.9 ng/L (Yang et al., 2011). Our data revealed a relatively higher level of estrogenic activity in surface water of Shanghai. This could be attributed to huge anthropogenic discharges into the aquatic environment as a consequence of Shanghai having the largest population density, industrial base and foreign trade port in China.

The average EEQ values of the 11 sampling sites at different sampling times and average EEQ values of 5 months at different sampling sites ranged from 8.12 to 88.46 ng/L and 26.36 to 58.08 ng/L, respectively (**Fig. 2**). In rainy seasons such as June, EEQ values of the 11 sampling sites ranged from 3.31 to 40.51 ng/L, with a mean value of 8.12 ng/L; in dry seasons such as December, EEQ values of the 11 sampling sites ranged from 54.06 to 127.6 ng/L, with a mean of 88.46 ng/L. The values
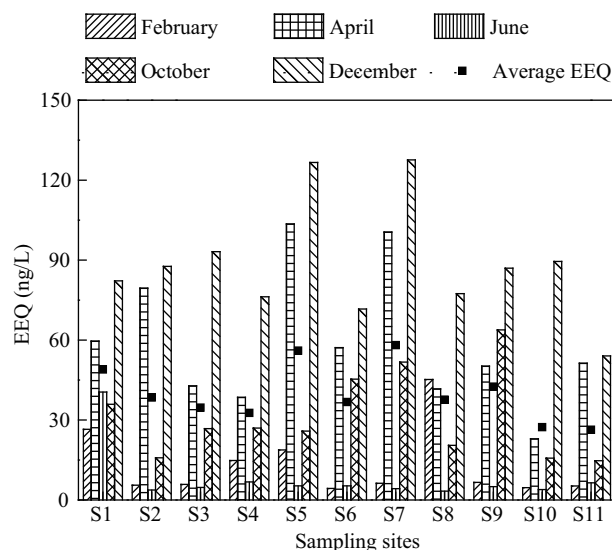

Fig. 2   EEQ of each sampling site in each month and average EEQ of each sampling site of five months.

of EEQ in rainy seasons were similar to those found in the Huangpu River in 2010 (Yang et al., 2010), in which the EEQ values ranged from 2.5 to 40.3 ng/L in the rainy season (April). The distributions of environmental estrogen in the Huangpu River at different sampling sites were also uneven. The sampling sites with the highest EEQ were S5 (mean 56.03 ng/L), which is located at one of the largest chemical industry areas of the city, and S7 (mean 58.08 ng/L), which is situated in the intensive livestock breeding and agricultural area. In contrast, water samples from the upper reaches of the Huangpu River (S10 (mean 27.33 ng/L) and S11 (mean 26.36 ng/L, located close to the water resource conservation area)) were found to have the lowest EEQ values. The sites of S3 (mean 34.66 ng/L) and S4 (mean 32.67 ng/L) located near the Shanghai Expo Park area also had low EEQ values. This might be attributed to the several rounds of comprehensive environmental rehabilitation of these sites since 2000.

2.3 Seasonal variation of EDCs, NDMA, and NDMA-FP in the Huangpu River

Although studies focusing on the occurrence of EDCs and NDMA have been published, few of them conducted multiple sampling events during one year, thus the seasonal variation data for these compounds are deficient. In our investigation, ten sampling events were conducted in 2012. As shown in **Fig. 3**, the overall target compound average levels at the 11 sampling sites around December were higher compared with those around June. Concentrations of E3, E2, t-NP, BPA, E1, NDMA, and NDMA-FP in December were 1.5, 13.0, 10.1, 10.9, 5.0, 2.0, 1.8, 5.2, and 10.9 times higher than those in June, respectively. While EE2 was not detected above the LOQ in all of the sampling sites in June, its average concentration was 41.36 ng/L in December. The total concentrations of target
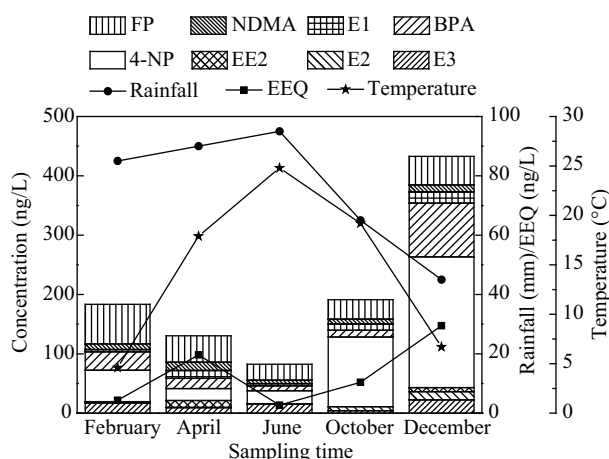
Fig. 3 Average concentrations of eight target compounds and EEQ of the 11 sampling sites, and average temperature and rainfall in each month

compounds and average EEQ values of the 11 sampling sites in December were 2.5 and 4.9 times higher than those in June, respectively. In addition, the number of detected target compounds and their detection rates were higher in December than those in June (**Table S1**). Only five target compounds (62% of the eight compounds) were detected in June, while eight were detected in December (100% of the eight compounds). Moreover, at the same sampling site, the total number of detected target compounds in December was greater than that in June (**Fig. 4**).

The different occurrences of target compounds among the five sampling months may be explained by the flow conditions of the river and the properties of the target compounds. The period from May to September is the season with typical flooding and high water level in the Huangpu River, and the period from November to April is the typical low water level season. In February, April, June, October, and December, the rainfall was 85, 90, 95, 65, and 45 mm, respectively, as shown in **Fig. 3** (Shanghai
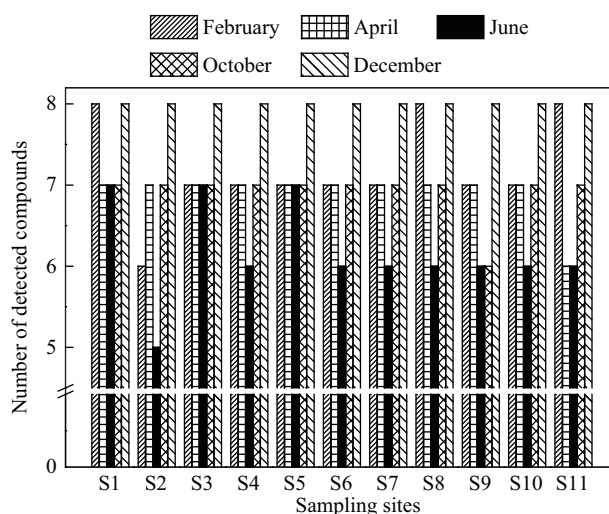

Fig. 4 Number of detected compounds in each month at the eleven sampling sites.

Water Authority, 2013). The total concentrations of target compounds from low to high were observed in the order of June, April, February, October, and December. They were consistent with the order of rainfall from high to low. The high flow rate conditions might result in extensive dilution of the concentrations of target compounds in the surface water. Moreover, bio- and photo-degradation of target compounds might be higher in summer than that in winter, due to the higher activity of microorganisms and strong sunlight in summer. Layton et al. (2000) reported that natural estrogens degraded more rapidly at higher temperatures in summer. Jonkers et al. (2005) also reported that higher concentrations of t-NP and their ethoxylates were found in colder seasons. In February, April, June, October, and December, the average temperature was 4.6, 17.9, 24.8, 19.2, and 6.7°C, respectively (Shanghai Meteo-rological Bureau, 2012). Therefore, lower concentrations were observed in June, and higher concentrations were observed in December.

It was noted that different dominant compounds were found among the different months for NDMA-FP and t-NP. In February, April, and June, the dominant compound was NDMA-FP, followed by t-NP, whereas the dominant compound was t-NP in October and December, followed by NDMA-FP (**Fig. 3**). The difference was likely due to the variance of compounds' consumption, the physic-ochemical behaviors of NDMA-FP and t-NP (such as biodegradation) and the flow conditions of the rivers in different months. He et al. (2013) reported that the aerobic biodegradation half-life of NP was 20 days at 22°C. Xin et al. (2013) reported that NP was almost totally removed and degraded in aerobic laboratory-scale activated sludge units at 28°C, but lowering the temperature led to decreased elimination capacities. Lower temperature led to more difficult biodegradation for t-NP, and thus contributed to the higher concentration detected in December than in June. Wastewater discharged in a river with a low flow rate may lead to an effluent-dominated stream, where the constituents of the wastewater discharged have a serious impact on the dominant compounds of the river. Because the flow rates of the Huangpu River in October and December are usually lower than those in February, April, and June, the higher levels of t-NP than that of NDMA-FP in October and December indicate that the occurrence of t-NP is more likely to be caused by the discharge of wastewater.

2.4 Spatial distribution of EDCs, NDMA, and NDMA-FP in the Huangpu River

Among all the sampling sites, the sum of average concen-trations of the eight target compounds in the whole year were found to be above 650 ng/L at sites S3, S5, S7, S8, and S9 (**Fig. 5**). The most contaminated sample was from site S9, with a concentration of 747.7 ng/L. Sites S3 and S5 are located in the commercial and industrial urban area,
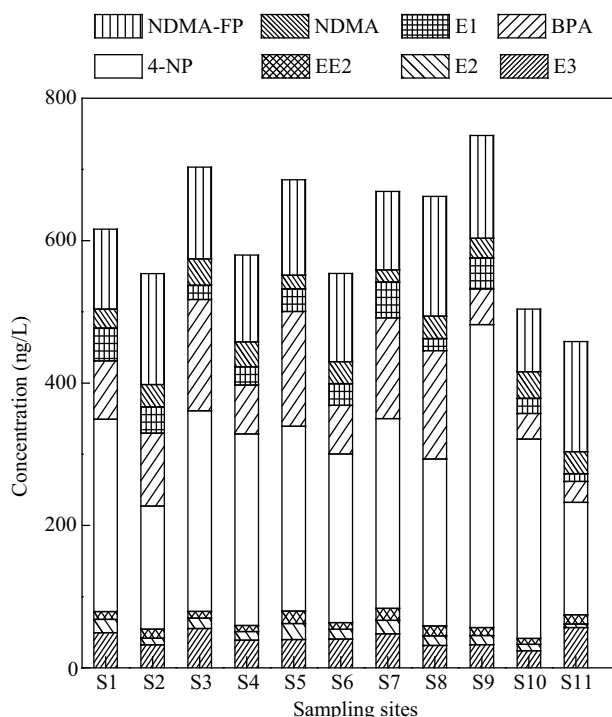
Fig. 5 Average concentrations of eight target compounds of five months at each sampling site.

while sites S7, S8, and S9 are located in the suburban area. The probable reason for high concentrations being found in both the urban area and suburban area may be that some of these target compounds, such as E1, E2, EE2, and E3, are used for or excreted by both humans and animals, leading to the release of these compounds into the surface water from both suburban and urban areas. It is estimated that 265,800 ton of livestock waste is produced from the intensive livestock farming and agricultural area around the upper reaches (suburban area) of the Huangpu River each year, and approximately 20% of livestock manure and 50% of urine are released into the environment without any treatment (Shanghai Water Authority, 2013).

A domestic sewage discharge could also explain the substantially high concentrations of NDMA-FP and NP at sites S3 and S5 which are situated near drainage outlets. Moreover, it was reported that higher NDMA concentrations were detected in prefectures that had higher levels of human activity (Asami et al., 2009). Therefore, it was possible to find high levels of EDCs and NDMA at sites S3 and S5.

Since agricultural runoff could include NDMA precursors such as herbicides, dispersed pollution from agricultural land may contribute to the NDMA precursors in sites S7, S8, and S9. Therefore, these activities should be regarded as area-specific or non-point sources of NDMA and NDMA-FP. Moreover, the site S7 is located in a tributary of the Huangpu River. The low water flow of this tributary might also account for the high levels of target compounds at site S7. The site S8 is at the downstream

of site S9 and located in the confluence of rivers. A possible reason for the levels observed at this site is that the tributary of the river provokes a dilution and results in different levels of target compounds at site S8 compared to site S9. Additionally, these compounds such as BPA and t-NP resist biodegradation and tend to transport much farther in the aquatic environment. Schreiber and Mitch (2006) also reported that NDMA precursors were degraded only slightly in wastewater-impacted river water.

Conversely, low levels of total eight target compounds for the whole year were found at sites S10 and S11, below 500 ng/L. This might be because the site S11 is located at Dianshan Lake, which is strictly protected as the source of the Huangpu River. The site S10 is situated in a tributary of the Huangpu River that flows through the protected area around Dianshan Lake, with low levels of pollutants.

In addition, it is worthy of noting that sites S6, S9, and S10 serve as drinking water sources and supply most of the raw water for Shanghai. However, comparable or higher EDCs, NDMA, and NDMA-FP levels were observed at sites S6 and S9 compared with the others. All these data indicate the urgency in controlling the micro-organics contamination of the Huangpu River.

3 Conclusions

All of the 11 sampling sites in the Huangpu River were contaminated by EDCs, NDMA, and NDMA-FP, with concentration levels at ng/L except for t-NP. Compared with E2 and EE2 concentrations, higher E1 and E3 concentrations were detected in the Huangpu River. The high values of EEQ suggest a high possibility of endocrine effects to the exposed organisms in the Huangpu River. The target compound concentrations in the order from low to high were observed in June, April, February, October, and December, which corresponded to the reverse of the order from high to low for rainfall and average temperature. NDMA-FP and t-NP were the dominant compounds of the eight target compounds. Higher concentrations of target compounds were observed in urban sampling sites near drainage outlets and also in suburban sampling sites where intensive livestock farming and agricultural areas were located. The above results indicate that attention should be paid to pollution control for EDCs, NDMA, and NDMA-FP in the catchment of the Huangpu River.

Supplementary materials

Supplementary data associated with this article can be found in the online vision.

R E F E R E N C E S

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Supporting materials

Distribution and seasonal variation of estrogenic endocrine disrupting compounds, N-nitrosodimethylamine, and N-nitrosodimethylamine formation potential in the Huangpu River, China

Ai Zhang, Yongmei Li[*], Ling Chen

State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China. E-mail: za19891207@163.com
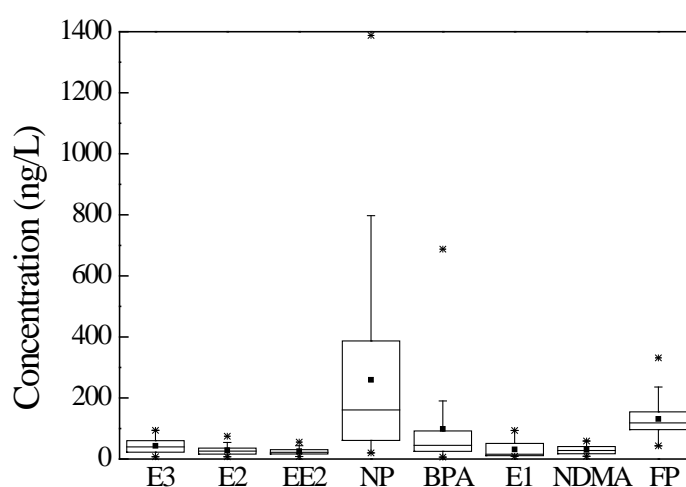
Fig. S1 Box-and-Whisker graphs of the concentrations of eight target compounds of eleven sampling sites along the Huangpu River from February to December in 2012. The horizontal line in each box is the median, the top and bottom of the box represent the 75 th and the 25 th percentile, respectively, and the whiskers define the 5 th and 95 th percentile observations

Table S1 Concentrations of target compounds detected in 11 sampling points collected from the Huangpu River in 2012 (unit: ng/L)

Sites	Sampling time	E3	E2	EE2	t-NP	BPA	E1	NDMA	NDMA-FP
	February	79.33	7.440	9.970	245.1	190.1	13.13	35.17	164.9
	April	22.73	ND	31.97	68.17	106.8	57.54	44.71	143.8
S1	June	77.03	35.08	ND	125.6	<LOQ	10.33	11.39	51.41
	October	12.78	15.00	ND	394.9	25.13	60.84	16.21	64.89
	December	55.64	35.15	12.52	516.9	87.72	89.03	26.32	135.9
	February	71.46	ND	ND	199.1	135.1	10.74	40.57	294.0
	April	22.43	ND	43.48	47.10	8.900	74.39	35.58	156.2
S2	June	ND	ND	ND	58.59	<LOQ	11.10	17.15	85.18
	October	7.540	10.35	ND	359.6	11.09	14.57	28.94	108.2
	December	60.56	35.71	20.48	200.0	356.2	74.35	34.50	135.4
	February	77.55	ND	<LOQ	233.6	146.4	11.11	33.37	189.8
	April	46.53	ND	30.60	72.74	14.08	10.16	47.27	122.6
S3	June	64.89	ND	<LOQ	47.72	12.69	9.340	51.38	96.14
	October	12.78	18.79	ND	386.8	36.96	21.63	27.69	81.83
	December	74.91	54.13	16.48	667.4	571.7	47.37	25.54	154.5
	February	38.92	ND	8.180	103.4	107.0	10.58	27.96	142.8
	April	38.33	ND	19.37	37.15	57.15	40.32	55.88	106.0
S4	June	38.63	ND	ND	67.21	51.85	17.44	16.25	96.16
	October	12.78	22.50	ND	339.3	27.10	11.33	29.10	107.1
	December	65.36	37.97	15.47	797.3	100.8	49.23	44.65	158.0
	February	43.53	ND	11.19	122.5	40.24	10.80	20.46	190.8
	April	15.03	16.97	55.37	78.83	20.97	51.30	<LOQ	149.8
S5	June	44.45	<LOQ	ND	53.55	18.77	12.66	9.720	98.44
	October	19.90	19.88	ND	257.4	38.19	15.62	22.17	90.58
	December	76.17	74.79	20.89	786.1	687.5	68.81	43.85	140.6
	February	25.40	ND	<LOQ	72.76	81.12	10.93	15.05	151.8
	April	22.79	ND	30.30	20.24	44.69	56.69	52.30	140.8
S6	June	78.44	ND	ND	43.66	52.06	10.20	24.62	87.62
	October	15.92	38.45	ND	405.5	76.39	18.02	18.05	102.2
	December	59.83	29.16	17.16	642.6	87.23	56.64	43.17	137.3
	February	47.24	<LOQ	ND	160.8	178.2	14.87	16.85	168.0
	April	38.78	ND	54.91	113.6	188.7	93.27	20.94	105.2
S7	June	34.94	ND	ND	46.64	40.87	10.18	9.160	43.40
	October	24.09	22.87	ND	340.4	54.21	84.33	22.61	103.1
	December	94.14	70.91	29.73	671.5	244.8	49.38	15.68	131.1
	February	49.92	12.78	22.00	178.0	30.47	10.54	15.35	331.4
	April	24.54	ND	25.29	60.58	41.91	28.45	54.09	187.0
S8	June	9.480	ND	ND	56.06	30.19	9.090	17.06	100.8
	October	17.60	16.32	ND	245.2	22.18	10.40	37.27	118.4

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	December	55.24	38.27	22.34	631.1	635.4	27.06	33.63	103.3
	February	33.28	ND	<LOQ	99.57	71.71	17.17	18.96	184.8
	April	29.28	ND	36.43	111.5	30.23	11.60	38.79	94.91
S9	June	40.38	ND	ND	61.00	26.79	12.03	12.47	76.00
	October	ND	32.33	ND	466.9	54.21	93.45	27.45	130.5
	December	59.45	32.50	18.94	1388	67.27	83.21	40.99	235.7
	February	43.68	<LOQ	ND	118.7	21.03	10.31	45.98	116.8
	April	9.510	ND	13.81	24.13	18.06	16.39	58.78	91.34
S10	June	16.64	ND	ND	54.36	19.14	10.41	14.09	52.60
	October	ND	15.04	ND	472.3	28.34	<LOQ	24.70	61.89
	December	50.47	30.18	27.21	730.9	92.16	70.04	43.09	117.0
	February	56.16	<LOQ	<LOQ	210.6	24.59	11.02	37.57	268.3
	April	35.57	ND	40.33	27.64	37.65	ND	55.09	163.2
S11	June	89.85	ND	ND	103.4	20.39	12.49	11.60	94.54
	October	14.45	7.69	ND	207.0	6.160	19.44	17.59	108.5
	December	87.22	16.25	25.17	240.6	58.56	11.88	31.96	138.8

Mean values are presented ($n = 2$, replicate samples taken at the same time). ND: not detected.

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