Screening of organic pollutants in environmental water in urban areas of Japan.

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Introduction:

The number of chemical substances newly produced or employed is increasing every year. In 2015, the 100 millionth chemical substance was registered with CAS. The number of CAS-registered substances increases every several seconds. More than 140 million substances were registered with CAS in April 2018. Currently, more than 100,000 registered substances are used in our daily lives, and most of them are discharged into the environment. Some of these chemical substances are harmful, so many environmental surveys to assess the impact on human health and the ecosystem are being done.

Today, the usual methods to analyze chemical substances in environmental samples are targeted analyses that analyze specified substances. Under the circumstances that the number of chemical substances discharged into the environment increases continuously, we cannot survey the actual situation or assess the environmental risks by only targeted analyses. As a solution to the problem, we are developing two kinds of method by liquid chromatography/quadrupole time-of-flight mass spectrometry (LC/Q-TOF/MS): (1) a screening method to analyze many chemical substances simultaneously and (2) nontargeted analyses to identify chemical substances.

Establishing these analysis methods will make it possible to analyze many pollutants diffused into the environment rapidly in case of such emergencies as natural disasters and accidents.

In this study, we analyzed environmental water samples from Japanese urban areas (Tokyo, Osaka, Hyogo, Nagoya, and Fukuoka) in screening methods and nontargeted methods using LC/Q-TOF-MS to detect many chemical substances simultaneously. In screening analyses, we surveyed chemical substances in urban water environments to detect pesticides and medicines and quantify them. For other substances, in nontargeted analyses, we tried to assign some peaks that were not subjected to screening analyses. We report the results of water environment analyses in each urban area.

Method:

For the screening targets, 503 pesticides, 328 pharmaceuticals, and 562 Pollutant Release and Transfer Register (PRTR) substances were selected for the screening targets. Standard solutions were measured by LC/Q-TOF-MS (Acquity H class, and Xevo G2-S, Waters Milford, MA, USA). ESI and the characteristic ions and retention times of the targets were determined with the response factors (Table 1). The screening was performed by liquid chromatography–high-resolution selected reaction monitoring (LC/HRSRM) and liquid chromatography–high-resolution selected ion monitoring (LC/HRSIM) with a mass accuracy of 5 mDa. High-intensity peaks of accurate mass of SRM chromatograms were identified with accurate masses and retention times, and the identified peaks were quantified with the response factors of the standard reagents.

The measurement conditions for the nontargeted analysis were also the same as in Table 1. Sample waters were collected in rivers in Tokyo (Nakagawa, at Hirai kobashi), Osaka (Yodogawa, at Johoku ohashi), Hyogo (Kakogawa, at Kakogawa Bridge), Nagoya (Horikawa, at Kizaemon Bridge), and Fukuoka (Tataragawa, at Nashima Bridge) in February 2017. We selected river downstream sampling sites to sample waters affected by sewage and many kinds of discharges.

The sample treatment scheme is shown in Fig. 1. Five hundred milliliters of water samples were filtered with a glass fiber filter, Grade GF/C. Filter residue as the suspended solid (SS) was twice extracted with acetone by sonication. Filtrate was passed through tandem Oasis HLB and Sep-Pak AC2 cartridges at a flow rate of 10 mL/min. Species collected in the cartridges were eluted with acetone and dichloromethane, in that order, which were concentrated, exchanged to (solvent), and subjected to LC/Q-TOF-MS.

Table 1. Analytical conditions of LC/Q-TOF-MS

LC : Waters Acquity Hclass			
Column	Waters CORTECS C18 (2.1×100mm, 1.6μm)		
Mobile phase	A : 1 mM CH_3COONH_4/H_2O	B : CH_3OH	
0→ 2min	A:95	B:5	
2→ 15 min	A:95→0	B:5→100	linear gradient
15→ 18 min	A:0	B:100	
18→ 22 min	A:95	B:5	
Flow rate 0.4 mL/min.	Column temperature	40 ℃	
Injection volume	5 μ L		

MS : Waters Xevo G2-S	
Cone voltage	20 V
Collision voltage	10-45 eV
Capillary voltage	0.75 kV
Cone gas flow rate	50 L/hr.
Desolvation gas flow rate	N_2(1100 L/hr.)
Source temperature	120℃
Desolvation temperature	500℃
Ionization mode	ESI-positive

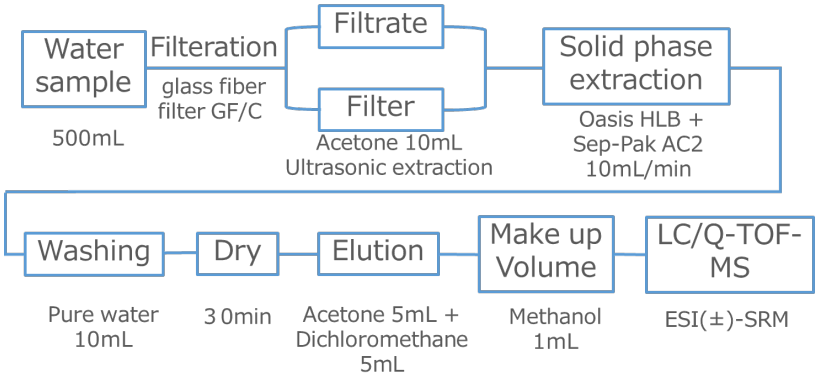

Fig. 1. sample treatment scheme

Result and discussion:

(1) Screening analyses

In the screening analyses, 12 kinds of pesticides, 36 kinds of pharmaceuticals and personal care products (PPCPs), and 11 kinds of the PRTR substances were found within a measured mass error of 5 mDa.

The pesticides, PPCPs, and phosphate esters were quantified with the response factors of corresponding standard reagents. In the quantified chemical substances, PPCPs were higher in the concentrations in Nagoya, and phosphate esters were higher in the concentrations in Tokyo, Osaka, and Fukuoka. The PPCPs highest in the concentrations were Fexofenadine (an anti-allergic drug), Theophylline (a bronchodilator), and Clarithromycin (an antibiotic), of which concentration ranges were 29.7–160 ng/L, 29.8–149 ng/L, and 18.7–144 ng/L, respectively. The concentration of Clarithromycin exceeds the PNEC. The concentrations of seven kinds of phosphate esters ranged from several ng/L to 200 ng/L. The results suggested that continuous investigation was necessary.

(2) Nontargeted analyses

The analysis results are shown in Table 2. In five cities, various kinds of industrial-use substances and pharmaceuticals were detected. In Tokyo, Osaka, and Hyogo, the frequency of detection of industrial materials was high, and the abundance was high. However, Nagoya and Fukuoka had a higher frequency of detection of pharmaceutical compounds. These two cities were affected by sewage treatment plants. Regarding the kinds of chemical substances to be detected, there were many common substances for industrial use in the five cities, and, for pharmaceuticals, the trends in Tokyo and the other four cities were different.

Table 2. Chemical substances found in river waters in five urban areas

Tokyo	Nagoya	Osaka	Hyogo	Fukuoka
2-A-2-M-1-PSA *1	Fexofenadine	DEHP *2	2-A-2-M-1-PSA *1	2-A-2-M-1-PSA *1
DEHP *2	Telmisartan	2-A-2-M-1-PSA *1	DEHP *2	DEHP *2
bis(DCHP)ethane *3	DEHP *2	N,N'-E(stearamide) *4	Dodecyloctaethylene	4-hydroxycoumarin
Cefoxitin	Chlorophyll A	1-MO-R-Glycerol *5	Polidocanol	Telmisartan
Fucoxanthin	Clarithromycin	Fexofenadine	N,N'-E(stearamide) *4	bis(DCHP)ethane *3
N,N'-E(stearamide) *4	2-A-2-M-1-PSA *1	Ricinolein	Laureth-5	Juvabione
Estradiol	Estradiol	4-hydroxycoumarin	1-MO-R-Glycerol *5	Cefoxitin
1-MO-R-Glycerol *5	Peridinin	Telmisartan	Trimethaphan	N,N'-E(stearamide) *4
Crotamiton	Levothyroxine	Diisoheptylphthalate	Telmisartan	Fexofenadine
Estriol	Argatroban	Docosanedioic acid	4-hydroxycoumarin	Clarithromycin
Dodecyloctaethylene	N,N'-E(stearamide) *4	Bezitramide	Fexofenadine	1-MO-R-Glycerol *5
Polidocanol	Travoprost	cocamidopropylbetaine	Ricinolein	Estradiol
4-hydroxycoumarin	Argatroban	Arterolane	Celgosivir	Nobiletin
Travoprost	1-MO-R-Glycerol *5	Dihydroqinghaosu Hemisuc	BSP	Androsta *6
Ricinolein	Erythromycin	4-hydroxycoumarin	Diisoheptylphthalate	Elaidoylamide
Fucoxanthin	Irbesartan	Estradiol	Docosanedioic acid	Fucoxanthin
Laureth-5	4-hydroxycoumarin	BSP	cocamidopropylbetaine	Estrone
Elaidoylamide	Bepotastine	Polidocanol	Elaidoylamide	Dodecyloctaethylene
Azithromycin	Bezitramide	Retosiban	4-hydroxycoumarin	Polidocanol
Sapacitabine	Crotamiton	Trimethylolpropane triacrylate	Levothyroxine	Lanosterol

*1 2-Acrylamido-2-methyl-1-propane sulfonic acid
*2 bis(2-ethylhexyl) phthalate
*3 bis(dicyclohexylphosphino)ethane
*4 N,N'-Ethylenebis(stearamide)
*5 1-Monooleoyl-Rac-Glycerol
*6 Androsta-4,16-dien-3-one

Industrial
Pharmaceuticals
Natural

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References:

1. Kadokami K. et al. (2012); *Anal. Sci.*, 28(12):1183-9
2. Hong T.C.C. et al. (2017); *Environ. Sci. Pollut. Res.*, 24(34):1-14