

**Fig. 2** Identification of substances registered in the private library by using the developed target screening system (A) 2,4,6-Trinitrotoluene and its metabolites (4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene) were detected in a groundwater. One liter of a sample was extracted with  $\text{CH}_2\text{Cl}_2$ , and then the extract was dehydrated and concentrated to 1 mL. (B) EPN was detected in an Welsh onion extract. After extracting 10 g of a sample with acetonitrile, the extract was cleaned-up with a graphitized carbon/aminopropyl-silicized silica-gel column, and then concentrated to 1 mL.

や測定装置に適した解析パラメーターを検討する必要がある。

以上より、本システムは機種に拘らず高精度な保持時間予測とデコンボリューション処理で得られたマススペクトル

に基づき、データベース登録物質をほぼ確実に同定できることを確認した。また、試料が夾雑物を多く含む場合でも、本システムの自動スクリーニングは市販の AIQS-DB と同等の同定能力を発揮し、分析者の目視確認と併せることで

同定精度の向上が期待できる。

### 3.5 実試料への適用

未知汚染物質を含む2種の実試料(地下水及びネギ)を用いて本システムの有効性を確認した。地下水試料は北九州市内の緑地で採取し、ジクロロメタン-液々抽出で得た最終試料液をターゲットスクリーニング分析した。その結果を Fig. 2 (A) に示すが、マトリックスの少ない地下水試料から爆薬のトリニトロトルエン(TNT)とその代謝物を検出した。試料採取地は過去に弾薬庫として使用されていた歴史があり<sup>17)</sup>、現在でも TNT やその代謝物によって地下水が汚染されていることが示された。

ネギ試料は、厚生労働省の一斉試験法<sup>18)</sup>で得た最終試料液を測定してスクリーニング解析した。地下水試料よりも夾雑物を多く含み、TIC にも多くのピークが出現したが、農薬のメタミドホスや EPN が検出された [Fig. 2 (B)]。

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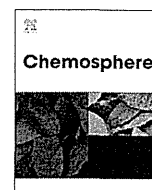
## Examination of Wide Use Target Screening System for GC/MS

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Since the number and volume of the chemical substances that we use has been increasing rapidly, effective tools are necessary to examine not only regulated chemicals, but also unregulated chemicals for evaluating the safety of foods and the environment and to investigate the causes of environmental pollution accidents. There are two conventional techniques to identify unknown substances in samples by GC/MS: mass spectra library search and automated identification and quantification system with a newly developed database (AIQS-DB). However, there are some restrictions in both techniques: a mass spectra library search needs standard substances for confident identification, and AIQS-DB needs a specific instrument. In this study, we investigated a novel target screening system for GC-MS by which every GC-MS on the market can certainly identify a large number of substances registered in a database without the use of standards. The developed system is composed of a freeware, "Automated Mass Spectral Deconvolution and Identification System" provided by National Institute of Standards and Technology and two private libraries [programed temperature retention indices (PTRI) and mass spectra]. By using *n*-alkanes as PTRI, under the same GC condition, the retention times of the chemicals in samples were exactly predicted with an error for less than 3 s in three different instruments from different GC/MS makers. From accurate predictions of the retention times and mass spectra, reliable identification was achieved with different instruments. Although the number of chemicals registered in the database is only 1000, since substance registration to the private libraries is easy, we can register thousands of substances in the database for achieving various purposes, such as finding causes of environmental pollution, evaluating the safety of foods and the environment and finding illicit drugs.

**Keywords:** GC/MS; AMDIS; identification; standard free; PTRI.



## Monitoring of 1300 organic micro-pollutants in surface waters from Tianjin, North China

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### HIGHLIGHTS

- First systematic investigation of 1300 chemicals in surface waters, China.
- 227 Organic micro-pollutants were found.
- Benzothiazoles, 2-naphthol and metformin were detected with high concentrations.
- Principal components analysis identified 4 factors for contamination origin.
- This comprehensive analytical method is a useful tool for environmental survey.

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### ABSTRACT

In spite of the quantities and species of chemicals dramatically increased with rapid economic growth in China in the last decade, the focus of environmental research was mainly on limited number of priority pollutants. Therefore, to elucidate environmental pollution by organic micro-pollutants, this work was conducted as the first systematic survey on the occurrence of 1300 substances in 20 surface water samples of Tianjin, North China, selected as a representative area of China. The results showed the presence of 227 chemicals. The most relevant compounds in terms of frequency of detection and median concentration were bis(2-ethylhexyl) phthalate (100%; 0.26  $\mu\text{g L}^{-1}$ ), siduron (100%; 0.20  $\mu\text{g L}^{-1}$ ), lidocaine (100%; 96  $\text{ng L}^{-1}$ ), antipyrine (100%; 76  $\text{ng L}^{-1}$ ), caffeine (95%; 0.28  $\mu\text{g L}^{-1}$ ), cotinine (95%; 0.20  $\mu\text{g L}^{-1}$ ), phenanthrene (95%; 0.17  $\mu\text{g L}^{-1}$ ), metformin (90%; 0.61  $\mu\text{g L}^{-1}$ ), diethyl phthalate (90%; 0.19  $\mu\text{g L}^{-1}$ ), quinoxaline-2-carboxylic acid (90%; 0.14  $\mu\text{g L}^{-1}$ ), 2-(methylthio)-benzothiazole (85%; 0.11  $\mu\text{g L}^{-1}$ ) and anthraquinone (85%; 54  $\text{ng L}^{-1}$ ). Cluster analysis discriminated three highly polluted sites from others based on data similarity. Principle component analysis identified four factors, corresponding to industrial wastewater, domestic discharge, tire production and atmospheric deposition, accounting for 78% of the total variance in the water monitoring data set. This work provides a wide reconnaissance on broad spectrum of organic micro-contaminants in surface waters in China, which indicates that the aquatic environment in China has been polluted by a large number of chemicals.

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### 1. Introduction

Water quality in China has deteriorated in the last decade as a result of the rapid expansion of industrialization and urbanization. For example, 100 tons of benzene, aniline, nitrobenzene and other toxicants were spilled into the Songhua River following a plant explosion in 2005 (He et al., 2013). In January 2013, more than 39 tons of aniline leaked into rivers in Shanxi province, posing a

great threat to the safety of drinking water for downstream provinces (Aredy, 2013). Tianjin is the fourth largest city in China, with a population of over 10 million. The city is located on the north west coast of Bohai Bay, and covers about 11 200  $\text{km}^2$  of land. As a coastal city, Tianjin suffers from a lack of water resources, and the wastewater that is discharged into surface waters from major industries without effective treatment has caused serious pollution to the aquatic environment. Surface waters passing through Tianjin also provide important drainage and wastewater discharge functions for Beijing City and Hebei Province, ultimately entering into Bohai Bay and pose a significant threat to local ecosystems.

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The presence of xenobiotic compounds especially organic micro-pollutants, such as pesticides, pharmaceuticals, phthalate esters and polycyclic aromatic hydrocarbons (PAHs) in aquatic ecosystems is a major concern worldwide, especially where drinking water supplies and amenity waters are contaminated by multiple chemicals for which human health based guideline values are not available (Kolpin et al., 2002; Zhang et al., 2007). Although most trace organic micro-pollutants are reported at low concentrations in the aquatic environment, the components of complex mixtures raise considerable toxicological concern since they have largely unknown combinative long-term effects on aquatic life and human health (Kümmerer, 2009). Also unknown is how many organic chemicals are used, although in the European Union, there are more than 100 000 registered chemicals, of which 30 000–70 000 are in daily use (EINECS, European Inventory of Existing Chemical Substances) (Loos et al., 2009). To date, most studies of trace organic chemicals in the aquatic environment have focused on a limited number of priority pollutants, because widespread screening for hundreds of organic chemicals in surface water is technically and financially challenging. Such screening, however, is urgently needed to better understand water quality and pollution sources in water resource limited areas, and to allow for the implementation of sustainable water use management strategies.

Recent progress in technology has improved the ability to detect and quantify a large variety of chemicals in environmental samples, although there are as yet few papers reported (Du et al., 2013; Hanh et al., 2013; Kadokami et al., 2009; Loos et al., 2009; Vryzas et al., 2009). In that context, Kadokami et al. (2005) developed a novel, automated screening gas chromatographic–mass spectrometric (GC–MS) method capable of operating in both selected ion monitoring (SIM) and total ion monitoring (TIM) in conjunction with a mass spectral database for simultaneous identification and quantification of nearly 1000 semi-volatile organic compounds (SVOCs). This GC–MS method was employed in this study, along with an analogous method utilizing liquid chromatography–time of flight mass spectrometry (LC–TOF–MS) in conjunction accurate mass database to allow for screening of around 300 compounds.

Targeted 1300 compounds are chemicals regulated by environmental protection laws and foods protection laws, and compounds that have been reported to be frequently detected in the aquatic environment and marker substances of pollution sources. Since we used the AIQS-DB (Kadokami et al., 2005), which can determine targets without the use of standard substances, we measured nearly 1000 substances by GC–MS. On the other hand, the number of substances measured by LC–TOF–MS is 300 because there is no AIQS-DB for LC–TOF–MS, we should use conventional measurement method for determination of the targets: preparing calibration curves before sample analysis, which restricts the number of substances measured simultaneously.

Monitoring programs for thousands of organic micro-pollutants inevitably generate complicated data matrix associated with a large number of parameters. Multivariate statistical techniques such as cluster analysis (CA) and principal component analysis (PCA) offer an attractive approach to interpret the datasets and refine the inventory information.

The aims of this study were to use the GC–MS and LC–TOF–MS methods to provide a more extensive picture of trace organic chemical contamination than might otherwise be obtainable using more conventional analytical chemistry, and in doing so to confirm the usefulness and effectiveness of the newly developed comprehensive analytical methods. The results obtained in this study provide valuable information to refine pollutants inventories and develop appropriate strategies for water sources management.

## 2. Materials and methods

### 2.1. Sample collection

A total of 20 sampling sites were selected, including locations in three watersheds (Jiyun River, Hai River and Dulu River) and two sewage canals (Fig. 1); these sites were chosen to represent the dominant surface water quality in Tianjin. Sites J1–J6 were located in the Jiyun River watershed; site J6 (Luann River) is the primary drinking water supply for Tianjin inhabitants. Eleven sites (H1–H11) were along Hai River watershed, the largest catchment in the northern China. Site D1 was in the Dulu River. Stations S1 and S2 were on the north and south sewage canals, respectively. Samples were taken from surface waters no deeper than 1.0 m depth using amber glass bottles in December 2013. All sampling vessels were pre-cleaned with acetone, purified water, and water from the point of collection. After collection, samples were kept in the dark and cooled with icepacks during transport to a laboratory where the water samples were stored at 4 °C for a maximum of 48 h until treatment.

### 2.2. Solid-phase extraction

Samples were prepared for measurement of both 949 SVOCs (Table S1) by GC–MS and 81 persistent organic pollutants (POPs, Table S2) by GC–MS/MS following the same method from Jinya et al. (2013). In short, surface water samples (1 L), spiked with surrogate standards (Table S3) were passed through a stack of multiple SPE disks (in ascending order, a glass membrane fiber disk (GMF 150, 47 mm, Whatman, Maidstone, UK), a styrene-divinylbenzene disk (Empore™ SDB-XD, 47 mm, 3 M Co., St. Paul, MN, USA), and an activated carbon disk (Empore™ AC, 47 mm, 3 M Co., St. Paul, MN, USA), after which the disks were subjected to vacuum for 30 min to remove water. The GMF and XD disks were eluted sequentially with acetone and dichloromethane, whereas the AC disk was eluted with only acetone. Both eluates were mixed and concentrated to 1 mL, then reconstituted to 5 mL with hexane. The final volume was reduced to 0.4 mL under a gentle stream of nitrogen, and mixed internal standards (Table S1) were added prior to instrumental analysis.

Samples were prepared for measurement of 303 polar and/or non-volatile organic chemicals (NVOCs, Table S4) by filtration of surface water (1 L) through a 47 mm glass microfiber filter GF/C (Whatman, Maidstone, UK) after adding surrogate standards (Table S3). The suspended solid (SS) was subjected to sonication extraction with methanol twice. The filtrate was passed through a PS 2 Sep-Pak cartridge and an AC 2 Sep-Pak cartridge (Waters Associates, Milford, MA, USA) at a flow rate of 10 mL min<sup>-1</sup>. The cartridges were eluted with methanol and dichloromethane. After combining the eluates and the extract from SS extraction, the mixture was concentrated to 50 µL under a gentle stream of nitrogen. Mixed internal standards (Table S4) were added and reconstituted to 1 mL with purified water prior to LC–TOF–MS analysis.

### 2.3. Chemical analysis

Monitoring of 949 SVOCs (Table S1) was performed with a GC–MS (Shimadzu, QP-2100 Plus, Kyoto, Japan) in both selected ion monitoring (SIM) and total ion monitoring (TIM). Target SVOCs information and GC–MS conditions were described in Tables S1 and S5, respectively. Total ion current chromatograms obtained by a GC–MS were treated with a novel Automated Identification and Quantification System with a GC–MS database (AIQS-DB) in order to identify and quantify of 949 SVOCs (Kadokami et al., 2005). GC retention times, calibration curves and standard mass

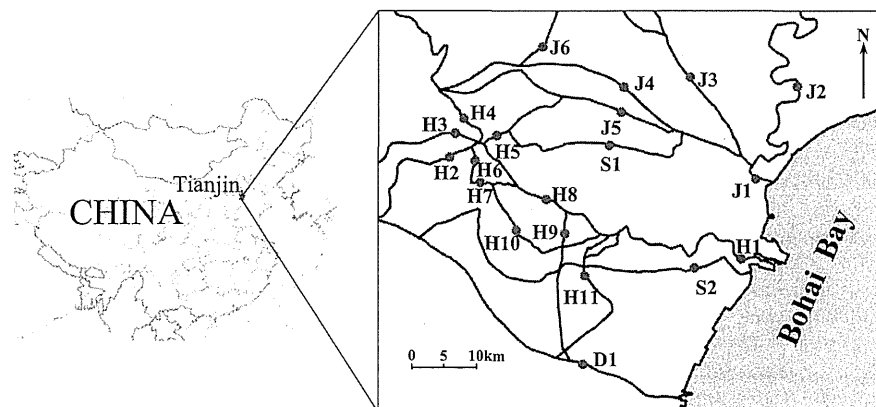


Fig. 1. Map of surface waters monitoring locations in Tianjin Municipality.

spectra of the 949 SVOCs were registered in the database, and the retention times of registered chemicals in actual samples were predicted from the retention times of *n*-alkanes (C9–C33) measured before sample analysis. Differences between predicted and actual retention times were less than 3 s, an accuracy that is nearly identical to that obtained by analysis of standard substances. The prepared samples were analyzed for 81 compounds including organochlorine pesticides and PCBs with a GC–MS/MS (TSQ Quantum XLS, Thermo Fisher Scientific, Yokohama, Japan) in selected reaction monitoring (SRM) mode. The details of compounds and instrument conditions were listed in Tables S2 and S6, respectively. The 303 NVOCs (Table S4) were measured with a LC–TOF–MS (Agilent 1200 HPLC Systems equipped with an Agilent 6220 TOF mass spectrometer, Tokyo, Japan). The LC–TOF–MS conditions were shown in Table S7.

#### 2.4. Quality control

All data were subjected to strict quality control procedures. Much attention was paid to reduce contamination throughout all the procedures. All the solvents were pesticide analysis grade and the sampling bottles with teflon caps were pre-washed with acetone and hexane prior to use. The milli-Q water was washed by hexane. The plastic materials were avoided through sample pretreatment and all glass wares were cleaned by acetone, hexane and water, then fried in 300 °C for 4 h. The lowest quantification limits of each chemical for GC–MS, GC–MS/MS, and LC–TOF–MS were calculated by dividing the lowest amounts on individual calibration curve by sample volume, which were 5–1000 ng L<sup>-1</sup>, 0.1–1.0 ng L<sup>-1</sup> and 4–200 ng L<sup>-1</sup>, respectively. Surrogate standards were spiked into all samples prior extraction to check recovery and matrix effects. For GC–MS/MS and GC–MS, average of recovery rates for 10 surrogates, which represented the same spectrum of physico-chemical characteristics as the chemicals in the analytical screen, including non-polar to polar chemicals, ranged from 67% to 135% (Table S3), while for LC–TOF–MS the average of recovery rates for 3 surrogate standards ranged from 64% to 85% (Table S3). The recoveries were not used to correct the concentrations of the detected compounds. Reagent blanks and procedure blanks were run in every 5 samples to check for cross-contamination and interference. The results of reagent and procedure blank were shown in Table S8. Although we tried precautions to avoid contamination, less than 6% of screened chemicals were still detected at concentrations higher than instrumental quantification limits in blank samples during GC–MS analysis. If the concentration of a target compound in a sample was 2 times higher than that in the blank,

the reported concentration in the sample was obtained by subtraction of blank concentration, otherwise it was not detected.

#### 2.5. Statistical analyses

The statistical analysis was performed using Microsoft Excel 2010 (Microsoft Japan, Tokyo, Japan) and IBM SPSS Statistics Ver. 20 (IBM Japan, Tokyo, Japan).

### 3. Results and discussion

#### 3.1. Overall occurrence of organic micro-pollutants

A total of 227 compounds were detected (Table S9), including sterols, antioxidants, pharmaceuticals and personal care products (PPCPs), PAHs, organophosphate ester flame retardants, plasticizers, and pesticides as well as other industrial chemicals in concentrations ranging from nanograms to micrograms per liter. The number of substances detected in the twenty surface waters ranged from 50 to 105. The total concentrations in south sewage canal (S1, 195 µg L<sup>-1</sup>) and north sewage canal (S2, 141 µg L<sup>-1</sup>) were several times higher than those observed in river samples from the Jiyun River, Hai River and Dulu River (which ranged from 7.7 µg L<sup>-1</sup> to 82 µg L<sup>-1</sup>). The lowest total residue concentration was found at H6 (7.7 µg L<sup>-1</sup>), followed by J3 and H10 with a total concentration of 10 µg L<sup>-1</sup> and 11 µg L<sup>-1</sup>, respectively. Ubiquitous residues with median concentration were cholesterol (2770 ng L<sup>-1</sup>), β-sitosterol (1210 ng L<sup>-1</sup>), bis(2-ethylhexyl) phthalate (DEHP) (259 ng L<sup>-1</sup>), siduron (198 ng L<sup>-1</sup>), coprostanone (126 ng L<sup>-1</sup>), lidocaine (96 ng L<sup>-1</sup>), antipyrine (76 ng L<sup>-1</sup>), hexachlorobenzene (2.1 ng L<sup>-1</sup>) and p,p'-DDD (0.70 ng L<sup>-1</sup>); the number of chemicals detected only once was 70.

#### 3.2. Sterols

Cholesterol was observed in every sample. Cholesterol is an important membrane component of animal cells, and is present in the feces of herbivores, omnivores and carnivores. It is therefore not diagnostic for any particular animal group. Coprostanol, however, is formed from cholesterol when animal tissues pass through an omnivores/carnivore's digestive system, and the presence of coprostanol and epicoprostanol are considered diagnostic for human fecal contamination. In that context, the elevated levels of coprostanol were perhaps not unsurprisingly observed in samples from the south sewage canal (S1 5.3 µg L<sup>-1</sup>), north sewage canal (S2, 4.9 µg L<sup>-1</sup>), although similar levels were observed at sites H3

(4.5  $\mu\text{g L}^{-1}$ ) and J2 (4.1  $\mu\text{g L}^{-1}$ ) both of which are surrounded by densely populated urban areas (Table S9). The lowest coprostanol concentration was found in J6 (not detected), a strictly protected drinking water source. Very low coprostanol concentrations were also observed at J3 (0.03  $\mu\text{g L}^{-1}$ ), a site located in a more remote northern area of Tianjin.

The  $\text{C}_{27}$ ,  $\text{C}_{28}$ , and  $\text{C}_{29}$  cholestane-based sterols found in fecal material are typically formed as reduction products of cholesterol and several higher molecular-weight isomers (campesterol, sitosterol, and stigmasterol) in the intestinal tracts of higher mammals. The sterol profiles of the feces reflect the diet of the source animal and conversions in the digestive tract, and sterol/stanol ratios have been used to identify the origin of fecal material. Grimalt et al. (1990) have suggested that a ratio of coprostanol/cholesterol greater than 0.2 indicates fecal pollution. In this study the coprostanol/cholesterol ratio was generally highest in sewage canals and urban regions, and low in rural and remote areas (Table S9). Further evidence for fecal contamination of the canals and urban waterways was provided by the coprostanol/(coprostanol + cholestanol) ratios (referred as  $5\beta/(5\beta + 5\alpha)$ ).  $5\alpha$ -cholestanol is formed naturally in the environment by bacteria and generally does not have a fecal origin (Martins et al., 2007). A joint evaluation of  $5\beta/(5\beta + 5\alpha)$  against coprostanol/cholesterol (Fig. S1) clearly showed a similar linear tendency between the two parameters. That the fecal matter was predominantly of human origin is also suggested by the coprostanol/(coprostanol + 24-ethyl coprostanol) ratios (mean ratio of 0.92; Leeming et al., 1998). Epicoprostanol, a coprostanol isomer, can be used as indicators of level of treatment since it is formed during the process of sewage degradation and found in human feces at very low concentrations (Martins et al., 2007). A cross-plot of the coprostanol/cholesterol ratio with the epicoprostanol/coprostanol ratio (Fig. S2) suggests that there are point sources of sewage discharge, although contamination at H11 may be attributed to old sewage pollution. That epicoprostanol was not detected at J1, J3 and D1 and suggests non-point source contamination by untreated feces.

### 3.3. Polycyclic aromatic hydrocarbons (PAHs)

Naphthalene was dominant individual PAH and occurred at the highest concentration at J6 (5.1  $\mu\text{g L}^{-1}$ ) and H5 (3.0  $\mu\text{g L}^{-1}$ ); these concentrations are higher than that found at the outlet of the sewage treatment plant discharging into the Tonghui River, Beijing, with a maximum concentration of 1.8  $\mu\text{g L}^{-1}$  (Zhang et al., 2004). That the Luan River drinking water supply (J6) also had high levels of naphthalene was surprising and the source needs further investigation. Low molecular weight PAHs (2–3 rings) were predominant in all the surface water samples and, on average, accounted for 78% of the total PAHs. Pies et al. (2008) suggest that a ratio of anthracene/(anthracene + phenanthrene) below 0.1 is diagnostic for a pyrogenic source for observed PAHs; otherwise the PAHs are of petrogenic origin. In this study the median anthracene/(anthracene + phenanthrene) ratio was 0.12 (ranged from ND to 0.17), which suggests the input of combustion products through the atmospheric deposition into Tianjin aquatic environment. The ratio of fluoranthene/(fluoranthene + pyrene) is also used to identify the PAH sources (De La Torre-Roche et al., 2009), and when calculated in this study the ratio in most surface waters (>0.5, except for sites J2, S1 and S2; Table S9) was indicative of PAHs from the burning of coal for heating during the winter in Tianjin City and industrial heavy fuel combustion.

### 3.4. Pharmaceuticals and personal care products (PPCPs)

Antipyrine (non-steroidal anti-inflammatory drug) and lidocaine (a local anesthetic) were detected in all the samples, with a mean

concentration of 95  $\text{ng L}^{-1}$  and 98  $\text{ng L}^{-1}$ , respectively. The concentration of antipyrine in this study was lower than that reported in sewage plants and rivers from Germany (Ternes, 1998), but slightly higher than that in surface waters from the Netherlands (de Jongh et al., 2012). Caffeine, quinoxaline-2-carboxylic acid, metformin and cotinine (a metabolite of nicotine) were observed in more than 90% of samples. Quinoxaline-2-carboxylic acid is used as a marker chemical for carbadox, production and usage of which has been banned in China since 2005. However, quinoxaline-2-carboxylic acid which was observed in the present study are suggestive of recent inputs because its half-life is only 8.5 d and the source of this chemical needs further investigation. The anti-diabetic drug metformin was determined at higher concentrations than other PPCPs at several sampling sites, with the highest value observed at S1 (20  $\mu\text{g L}^{-1}$ ), followed by H3 (2.9  $\mu\text{g L}^{-1}$ ) and H1 (2.4  $\mu\text{g L}^{-1}$ ). Site S1 may be impacted by the discharge from metformin production upstream whereas sites H3 and H1 are both located in urban areas and may indicate large amounts usage of this drug within Tianjin's large population. To our best knowledge, this is the first report concerning the occurrence of metformin in surface waters in China, although, similar metformin concentrations have been reported in surface waters and wastewater effluents in Germany (Scheurer et al., 2012). The other 4 widely detected PPCPs in terms of mean concentration were clarithromycin (frequency of detection (FOD) 75%; 25  $\text{ng L}^{-1}$ ), roxithromycin (FOD, 75%; 57  $\text{ng L}^{-1}$ ), acetaminophen (FOD, 70%; 395  $\text{ng L}^{-1}$ ) and diethyltoluamide (FOD, 70%; 40  $\text{ng L}^{-1}$ ). The high concentration of acetaminophen observed in this study was reasonable because it has been listed as one of the four most often-used anti-inflammatory pharmaceuticals in China (Peng et al., 2008).

### 3.5. Domestic and industrial chemicals

Elevated levels of sum of four benzothiazoles (benzothiazole, 2-(methylthio)-benzothiazole, 2(3H)-benzothiazolone and 2-methylbenzothiazole) were found in the north sewage canal (S1, 89  $\mu\text{g L}^{-1}$ ), J1 (61  $\mu\text{g L}^{-1}$ ) and J5 (9.7  $\mu\text{g L}^{-1}$ ). Sine benzothiazoles were used as vulcanisation accelerator, the high concentration observed in above three sites may be ascribed to wastewater discharge, in this case from tire manufacturing industries located upstream. Phthalic acid esters (PAEs) are widely used as plasticizers to improve flexibility and workability and recent toxicological studies have demonstrated the potential of the most important phthalates to disturb the human hormonal system and human sexual development and reproduction (Zheng et al., 2014). Among the six detected PAEs, DEHP and diethyl phthalate (DEP) were found in >90% of surface water samples, with a mean concentration of 0.58  $\mu\text{g L}^{-1}$  and 0.25  $\mu\text{g L}^{-1}$ , respectively, although at relatively low concentrations compared to surface water in USA and Europe (He et al., 2013). Triphenyl phosphate (TPP), as organophosphate flame retardant, was detected in >95% sampling sites, with a mean value of 88  $\text{ng L}^{-1}$ . TPP is acutely toxic to aquatic organisms and is a suspected neurotoxin (Li et al., 2014); its concentration in the present study is comparable to those reported in river water from Austria (Martínez-Carballo et al., 2007). The chemicals 4-nonylphenol and bisphenol A had mean concentrations of 565  $\text{ng L}^{-1}$  and 25  $\text{ng L}^{-1}$ , respectively. The high levels of 4-nonylphenol in the present study are in good agreement with a previous report (Jin et al., 2004) and indicate the widespread application of alkylphenol ethoxylates. However, the concentration of 4-nonylphenol and bisphenol A in this study was much lower compared to that in surface waters from Germany (Bolz et al., 2001).

A total of 36 industrial compounds were detected in surface waters of Tianjin. Of the chemicals detected in >60% samples were dibenzofuran (85%), biphenyl (75%) and quinoline (70%), with a mean value of 85  $\text{ng L}^{-1}$ , 85  $\text{ng L}^{-1}$  and 155  $\text{ng L}^{-1}$ , respectively.

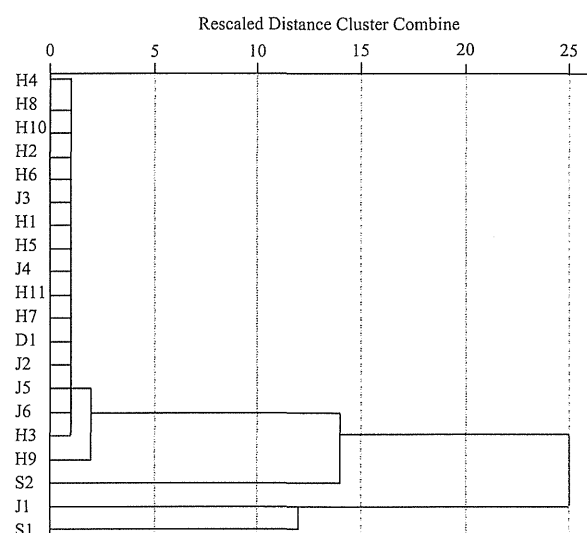
The results reflect that Tianjin is a diversified economic hub in northern China. Tianjin's pillar industries are electronics and information technology, automobiles, bio-tech and pharmaceuticals, metallurgy and petrochemicals industries. Many of these manufacturers could potentially discharge various industrial related pollutants into the environment. Total concentrations of industrial compounds over  $1 \mu\text{g L}^{-1}$  was observed at J1, J5, J6, H2, H5, S1, S2 and D1. The maximum concentration of industrial compounds was found in south sewage canal ( $65 \mu\text{g L}^{-1}$ ), which was influenced by high concentrations of 2-naphthol ( $51 \mu\text{g L}^{-1}$ ). It was not surprising since Tianjin was an important production base for 2-naphthol. The high concentration of 2-naphthol only found in south sewage canal can be attributed to the wastewater discharge from 2-naphthol manufacturer which was close to our sampling site.

### 3.6. Multivariate statistical analysis

The detected 227 compounds were divided into 18 groups (Table 1), and then hierarchical cluster analysis was applied to evaluate the spatial variation of these 18 parameters. Squared Euclidean distance was calculated and the dendrogram was rendered in Fig. 2. The results significantly separated J1, north sewage canal (S1) and south sewage canal (S2) from other sampling sites at ( $D_{\text{link}}/D_{\text{max}} \times 25 < 5$ ). It should be noted that the high concentrations observed at J1 is likely affected by the influx from north sewage canal since this site is located in downstream of the confluence (Fig. 1). Sites J1, S1 and S2 represent sites at which the pollution source is wastewater. Principal component analysis (PCA) on the same data used for spatial cluster analysis renders four varifactors with eigenvalues higher than 1.0 accounting for 78% of total variance (Table 1). Varifactor 1 (VF1) explained 31% of total variance and was correlated with (loading  $>0.7$ ) 6 parameters including intermediates for dyes, chemical intermediates used in organic synthesis, disinfectants, fragrances, fire retardants and pesticides associated with wastewater of industrial, household/business origin and agriculture runoff. VF2 accounting for 20% of total variance showed high correlations (loading  $>0.8$ ) for leachate from tires, PPCPs and benzothiazoles and this principle component mainly represent the tire manufacture source. Important contributors for VF3 were cholesterol, phytosterol, zoosterol and plasticizers; accounting for 15% of total variance, these chemicals were mainly related to sewage sources. VF4 was dominated by PAHs and

**Table 1**  
Principle components loadings matrix for data of surface waters in Tianjin.

Variable	PC1	PC2	PC3	PC4
Disinfectant	0.98	-0.01	0.12	-0.03
Intermediate in organic synthesis	0.97	0.02	0.12	0.04
Intermediate for dyes	0.96	-0.02	0.11	0.09
Fragrance	0.94	-0.05	0.06	-0.01
Fire retardant	0.79	0.14	0.22	-0.04
Pesticide	0.72	0.10	0.50	0.00
Leaching from tire	0.05	0.97	0.03	0.03
PPCPs	-0.04	0.96	0.21	-0.01
Benzothiazole	-0.09	0.88	-0.05	-0.05
Antioxidant	0.53	0.60	-0.25	-0.02
Phytosterol	0.02	-0.24	0.84	-0.18
Cholesterol	0.13	0.33	0.79	-0.10
Plasticizer	0.43	-0.05	0.67	0.03
Zoosterol	0.35	0.49	0.63	-0.05
Intermediate for resin	-0.09	0.08	0.01	0.94
PAH	0.11	-0.16	-0.22	0.91
Fatty acid methyl ester	0.00	-0.12	-0.05	-0.05
Industry	0.28	0.25	-0.04	0.35
Eigenvalues	6.3	3.5	2.7	1.6
% Variance explained	31	20	15	8.6
% Cumulative variance	35	54	70	78



**Fig. 2.** Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for 20 sampling locations.

intermediates for plastic resins; accounting for 8.6% of total variance, their origins are atmospheric deposition and resin production.

## 4. Conclusions

The surface waters in Tianjin are heavily polluted with a large number of organic micro-pollutants. The causes of pollution are industrialization, modernization and urbanization, being experienced by this region and the current management systems for controlling contaminants discharge cannot catch up these the rapid expansion of these factors. In the present study it was confirmed that monitoring for 1300 organic micro-pollutants provided a much more holistic picture of pollution and revealed that all surface waters in Tianjin were more or less impacted by anthropogenic activities, albeit that the distribution of each chemical class varied among sample locations as a result of population density, geographic condition, level and distribution of industry and agriculture. In contrast to a study on Tokyo Bay (Pan et al., 2014), this study suggests that insufficient treatment efficiency in sewage treatment plants is a major cause of the pollution in the canals. For the three watersheds in Tianjin, chemicals of domestic origin, sterols and pesticides were significant contributors to pollution profiles, even in relatively remote areas; this is consistent with studies in Japan (Pan et al., 2014) and Europe (Loos et al., 2009). Overall, the comprehensive data obtained provides valuable information for refining chemical inventories and technical support for developing sustainable water strategies towards these contaminants.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.11.025>.



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# 化学物質網羅分析法の開発と途上国の環境調査

Development of comprehensive analytical methods for  
chemicals and environmental survey in developing countries

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## 摘 要

開発済みの GC/MS (ガスクロマトグラフィー/質量分析法) 及び LC/TOF-MS (液体クロマトグラフィー/飛行時間型質量分析法) 向けの全自動同定・定量データベースシステムを活用して 2 種の水試料用網羅分析法を開発した。半揮発性化学物質の網羅分析は、液々抽出又はタンデム型の固相抽出を用いて広範囲の極性から構成される 1,000 物質の大半を定量的に分析できた。同様に 300 種の難揮発性化学物質もタンデム型の固相抽出を用いることで、抽出が難しい水溶性物質を定量的に抽出し、精確に分析できた。両手法を用いて、中国、ベトナム及び日本の河川を調査した結果、検出物質の多くが共通していた。このことから、経済のグローバル化により化学物質汚染も世界共通となっていることが確認された。一方、検出濃度は中国とベトナムが日本と比べて大幅に高かった。これは、化学物質の使用・管理・廃棄が適切に行われていないためであろう。以上の結果から、途上国の化学物質汚染の把握には、網羅分析が有効なツールであることが確認された。

キーワード：液体クロマトグラフィー/飛行時間型質量分析法, 環境汚染,  
ガスクロマトグラフィー/質量分析法, スクリーニング分析,  
有害化学物質

Key words : LC/TOF-MS, environmental pollution, GC/MS, screening analysis,  
micro-pollutants

## 1. はじめに

米国化学会 (American Chemical Society) の情報部門である Chemical Abstracts Service のホームページには、これまでに全世界で合成された化学物質の数が表示されている<sup>1)</sup>。その数は、2014 年 3 月 31 日現在 85,146,000 であり、2013 年 3 月の 7,100 万からわずか 1 年で 1,400 万も増加している。このような近年の加速度的な物質増加は、全て人類の知的探求心と幸福・繁栄を目指したものであり、有用な化学物質は製造・市販されて身の回りで使用され、人類の繁栄と豊かな生活を支えている。しかし、その生産・使用量の増加にともない、一部の化学物質によるヒトや生態系への影響が報告されている。『沈黙の春』<sup>2)</sup>では DDTs (Dichloro-diphenyl-trichloroethane, ジクロロジフェニルトリクロロエタン類) による生態系への影響、PCBs (Polychlorinated biphenyls, ポリ塩化ビフェニル類) ではヒトや野生生物への影響、

フロンではオゾン層の破壊など、当初は低毒性・有用と思われていた化学物質によるヒトや生態系への影響が数多く報告され、地球環境全体への影響も懸念されるようになった。特にリスクが高い残留性有機汚染物質 (POPs; Persistent organic pollutants) については、2004 年に残留性有機汚染物質に関するストックホルム条約で全世界での製造・使用が禁止 (制限) され、POPs 指定物質も当初の 12 物質 (群) から 22 物質 (群) へと増加している<sup>3)</sup>。

人類が被害を受けてきた物質は、各種基準が定められて日常的にモニタリングされ、安全が担保されている。しかし、全世界で使用されている物質は 10 万種にのぼるといわれており<sup>4)</sup>、不適切な使用、地震や事故などでの流出、意図的・非意図的な廃棄などにより汚染が生じるリスクは高い。また、極低濃度の長期ばく露でヒトや生態系に予期しない影響を与えるおそれもある。特に、経済発展優先の発展途上国では、人々の化学物質に対する関心や知識が

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乏しく、化学物質管理が不十分であり、廃水や廃棄物の処理も充分に行われていないため、化学物質によるヒトの健康や生態系への影響リスクは日本などの先進国と比較して大きいと考えられる。このような途上国での環境悪化を防止するには、規制の有無にかかわらず可能な限り多くの物質の環境での存在を調べ、その経時的な変化や環境リスクを把握しておく必要がある。しかし、従来の手法で数多くの物質を分析するには、膨大なコストと労力が必要であり、途上国での実施は困難である。このような状況に対応するため、筆者らは1回の分析で数百～数千種の物質を分析できる網羅分析法の開発を進めてきた<sup>5), 6)</sup>。本稿では、著者らが開発した全自動同定・定量データベースシステム(AIQS-DB; Automated Identification and Quantification System with a Database)、及び水試料中の半揮発性物質と水溶性物質の前処理法を説明するとともに、両者を組み合わせた網羅分析法で実施した発展途上国の環境調査結果を紹介する。開発した2種の分析法を用いることで試料中の1,300物質の分析が可能であり、化学物質の環境汚染の全体像の把握と環境リスクを推計して、その結果を踏まえて必要ならば詳細な調査へ進むことができる。

## 2. 網羅分析法の開発

化学物質の分析は、試料の前処理と機器分析から構成される。分析機器で対象物質が測定できなければ、前処理法の開発もできない。そのため、分析法の開発では最初に対象化学物質の測定法を検討する。環境試料の中には対象化学物質以外の多くの夾雑物が含まれ、対象物質は極微量であるため、測定機器は高感度・高選択でなければならない。現時点においてこのような性能を有する機器として、クロマトグラフィーと質量分析法を組み合わせた装置が最適である。揮発性、又は熱をかけて揮発する物質の測定には、ガスクロマトグラフィー/質量分析法(GC/MS; Gas Chromatography - Mass Spectrometry)が、GC/MSが適用できない難揮発性・熱分解性物質には液体クロマトグラフィー/質量分析法(LC/MS; Liquid Chromatography - Mass Spectrometry)が用いられる。そこで筆者らは、GC/MSとLC/MSを用いた2種類のAIQS-DBを開発した<sup>5), 6)</sup>。

MSの測定法としては、ある質量範囲の全てのイオンを測定するスキャン法(TIM; Total Ion Monitoring)、特定のイオンを測定する選択イオン検出法(SIM; Selected Ion Monitoring)や選択反応検出法(SRM; Selected Reaction Monitoring)が通常用いられるが、数百～数千の化学物質を一斉に分析する網羅分析には、人間の指紋に相当するマススペクトルが得られるTIMが適している。

GC/MSは、安価で環境や食品分析で最も使用さ

れているキャピラリーGC/四重極型MSを用いた。キャピラリーGCは高いピーク分離能をもつため、整数単位の質量分解能の四重極型MSでも確実に物質同定ができる。一方、LC/MSは、LCのピーク分離能がキャピラリーGCに比べて劣るため、小数点第3位までの質量数を精確に得ることができる飛行時間型質量分析計(TOF-MS; Time-of-Flight Mass Spectrometer)を検出器に採用した。これにより、保持時間と精密質量スペクトルを組み合わせることで確実に物質を同定できる。また、イオン化法には、中～高極性物質の測定に適したエレクトロスプレーイオン化(ESI; Electrospray ionization)のポジティブモードを採用し、カラムも一般的なODS(Octadecyl-silane, オクタデシルシラン)(C18)カラムを用いることとした。

GC/MSやLC/MSによる試料測定では、測定時の保持時間や装置感度(検量線)を確認するために対象物質の標準品の測定が必要であるが、筆者らは、GC/MSにおける保持時間や検量線の傾きを一定にする手法を考案し、データベース化することで試料測定時の標準品を不要とすることができた<sup>5)</sup>。これまでにGC/MS向けAIQS-DBには約1,000種の半揮発性物質が、LC/MS向けAIQS-DBには300種の難揮発性物質が登録されている。データベースには新規物質登録が容易であるため、理論的には採用した条件で測定可能な物質は全て測定できる。また、別の測定条件で新しいデータベースを構築すれば、半揮発性・難揮発性物質以外の化学物質も網羅分析可能である。

網羅分析法の開発に当たっては、GC/MS及びLC/MSのそれぞれのAIQS-DBで測定可能な物質を全て分析できる手法を検討した。

### 2.1 GC/MSを用いた半揮発性化学物質の網羅分析

GC/MS向けAIQS-DB登録1,000物質には、水溶解度の大きい、すなわちオクタノール-水分配係数(log Kow)の小さい物質(log Kow 0以下)からlog Kowが10以上の高疎水性物質が含まれている。このような広範囲の極性から構成される物質群を単一の手法で水試料から抽出するのは、実際には困難である。特に、水溶解度の大きい物質を水から分離することは難しい。液々抽出では、Dichloromethane(ジクロロメタン)が広い極性範囲の物質群の一斉抽出に最も適した溶媒であり、EPA Method 625<sup>7)</sup>やStandard Methods for the Examination of Water and Wastewater<sup>8)</sup>でも採用されている。著者らも液々抽出にジクロロメタンを採用して、大半の登録物質を定量的に分析できた<sup>9)</sup>。ただ、近年は有害な溶媒(特に、ジクロロメタンは発がん性)を大量に使用する液々抽出の代わりに固相抽出が使用されている。そこで、カートリッジ型と大量の試料に適したディスク型の両方を用いて網羅分析に適した固相を検討した。その結果、ポリマーと活性炭を組み合わせたタンデム抽出法が最も回収率がよいことが確認された<sup>10)</sup>。

### 2.1.1 分析法<sup>10)</sup>

ディスク型での分析法のフローチャートを図1に示す。真空マニホールドにガラス繊維ろ紙 GMF150 (Whatman 社), エムポア™ ディスク SDB-XD 及び エムポア™ カーボンディスク AC(3M 社)を積層し, 緩衝液を加えて pH7.0 に調整した水試料を通水する。その後, 精製水で固相を洗浄し, 窒素ガスを30分以上通して脱水する。次に, GMF150と SDB-XD を重ねたまま Acetone(アセトン)とジクロロメタンを流して溶出し, AC はアセトンで溶出する。全ての溶出液をあわせ, 窒素ガス気流で約 1 mL まで濃縮後, Hexane(ヘキサン)を添加して Anhydrous sodium sulfate(無水硫酸ナトリウム)で脱水する。このヘキサン溶液を窒素ガス気流で約 1 mL まで濃縮し, 内標準を加えて GC/MS で測定する。

### 2.1.2 添加回収試験

AIQS-DB 登録物質は, 広範囲の物理化学的性質から構成されているため, それらを構造や官能基が異なる 57 物質群に分け, 各物質群から 1 物質以上計 202 物質(沸点: 146~536°C, log Kow: -0.65~15.07)

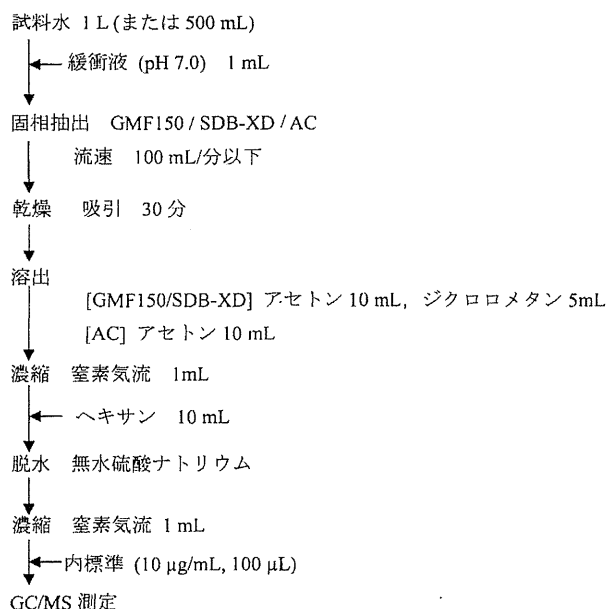


図1 半揮発性化学物質の網羅分析法フローチャート。

をモデル物質として選び, 精製水に各 0.1 µg/L になるよう添加して回収試験を行った。その結果を図2に示す。202 物質のうち, 191 物質が 50% 以上の回収率を示し, その平均回収率は 96% (50%~118%) であった。低回収率の物質は, 水酸基やアミノ基などの極性官能基を分子内に 2 個以上もつ物質, Phenol (フェノール) など水中で解離する物質, Benzidine (ベンジジン) など分析中に酸化する物質, 水溶性が非常に大きい物質などであり, 多くが log Kow 1 未満の高極性物質であった。これらの物質は抽出率が低だけでなく, AIQS-DB の GC 条件では測定も難しい物質である<sup>11)</sup>。統計学的に求めた本分析法の検出限界は, 平均 0.034 µg/L (0.011~0.078 µg/L) であった。さらに, 河川水, 海水及び下水道放流水を用いた添加回収試験でも精製水と同様な結果が得られ, 本分析法が環境分析に充分使用できることが確認された。

### 2.2 LC/TOF-MS (Liquid Chromatography – Time-of-Flight Mass Spectrometry) を用いた難揮発性物質の網羅分析

LC/MS 向け AIQS-DB には, 農薬や医薬品・パーソナルケア製品 (PPCPs; Pharmaceutical and Personal Care Products) を中心に約 300 物質が登録されている。登録物質の多くは, log Kow が小さい水溶性物質であるが, 一部は疎水性物質も含まれている。そのため, GC/MS での網羅分析と同様に複数の固相を連結したタンデム型 SPE (solid-phase extraction, 固相抽出) を検討した。市販の 5 種類の固相を用いてモデル物質の回収率を検討した結果, Sep-Pak Plus C18 (オクタデシルシリル充填剤, Waters 社) は疎水性物質に最適であり, Sep-Pak PS-2 (スチレンジビニルベンゼンポリマー, Waters 社) は疎水性から弱親水性物質までに適し, Oasis HLB Plus (親水性ポリマー, Waters 社) や Aquasis PLS-3 (親水性ポリマー, GL Science 社) は Sea-Pak PS-2 に比べて水溶性の高い物質に適していた。また, 水溶性が非常に大きい物質の抽出には Sep-Pak AC-2 (活性炭, Waters 社) が有効であることが分かった。これらの結果を踏まえて, Sep-Pak PS-2 と Sep-Pak AC-2

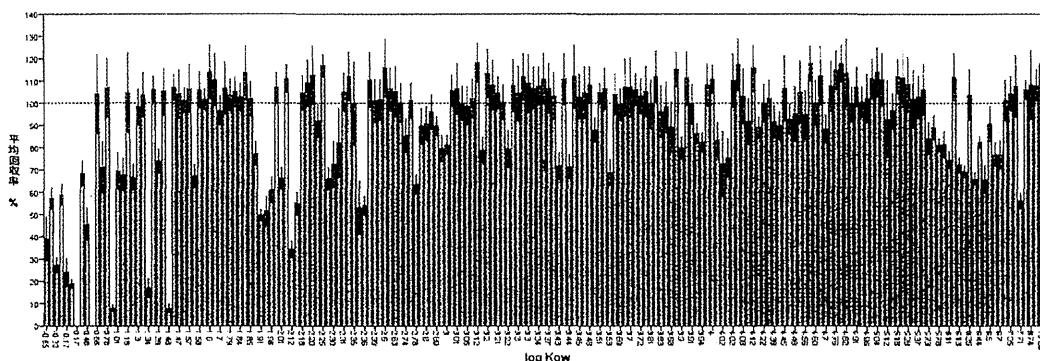


図2 半揮発性化学物質(横軸)の添加回収結果。バーは回収率の平均値の95%信頼区間を示す。

を組み合わせたタンデム抽出法を採用することとした。

採用した固相はカートリッジタイプであるため、加圧型と吸引型の2種の固相抽出装置を使用することができる。加圧型は自動化が可能、浮遊物質による目詰まりがしにくい、一定流量で通水が可能などの利点があり広く使われているが、疎水性の大きい物質は装置の流路などに吸着して回収率が低下する可能性がある。モデル化合物を用いた事前検討でも、 $\log Kow$ が4以上の疎水性物質の回収率において低い結果が得られた。また、同様の高疎水性物質の回収率の低下が、LC/TOF-MS注入試料のろ過に用いるシリンジフィルターでも起こることが判明した。そこで、固相抽出装置には吸引式を使用することとし、最終試料液はメタノール溶液としてシリンジフィルターでろ過後、精製水で定容にすることとした。

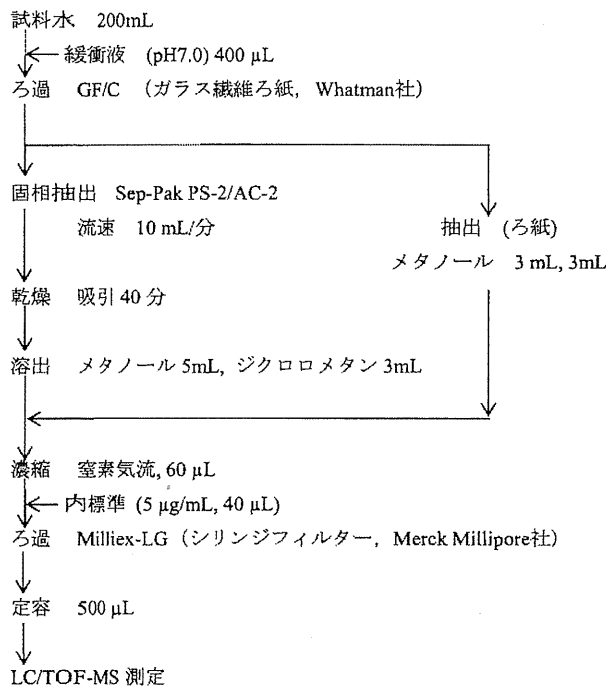


図3 難揮発性化学物質の網羅分析法フローチャート。

## 2.2.1 分析法

難揮発性物質の分析法のフローチャートを図3に示す。Sep-Pak PS-2をSep-Pak AC-2の上に取り付け、吸引型の固相抽出装置にセットする。これに試料水200 mLを通水し、精製水で固相を洗浄した後、吸引を続けて脱水する。Sep-Pak AC-2とSep-Pak PS-2を入れ替え、Sep-Pak AC-2側からアセトンとジクロロメタンを流して溶出する。溶出液を窒素気流で濃縮して内標準を添加した後、シリンジフィルターでろ過し、精製水で定容としてLC/TOF-MSで測定する。

## 2.2.2 添加回収試験

添加回収試験は、LC/MS用のAIQS-DB登録物質の中から広範囲の物理化学的性質をもつ( $\log Kow$  -2.2~5.03)126農薬をモデル物質として選定し、精製水に各0.1 µg/Lになるよう添加して図3に従って行った。その結果を図4に示す。126農薬のうち、105農薬の回収率が目標とした70%を上回り、平均回収率は91%であった。低回収率の物質は、アシュラムなどの水溶性が非常に大きい物質や $\log Kow$ が4以上の高疎水性物質であった。高疎水性物質の回収率が低い原因は、シリンジフィルターへの吸着と考えられた。なお、図4において $\log Kow$ が2.5前後に低回収率の物質(Hexythiazox, ヘキシチアゾクス)があるが、この物質の保持時間は非常に大きく、実際の $\log Kow$ は文献値の2.53<sup>12)</sup>より大きい可能性がある。装置検出限界を試料換算して求めた検出限界は、0.01~0.5 µg/Lであった。以上から、本分析法は $\log Kow$ が4未満の物質の環境分析に充分使用できる精確さと感度を有していることが確認された。

## 3. 発展途上国の環境試料への適用

### 3.1 中国長江<sup>13)</sup>、天津市河川及びベトナム河川<sup>14)</sup>の半揮発性化学物質汚染

GC/MS向けAIQS-DB登録物質は、国内外の環境関連法規の規制物質、残留農薬及び環境から検出例のある物質である。また、発生源の指標となるマーカー物質も含まれている。よって、検出物質の種類

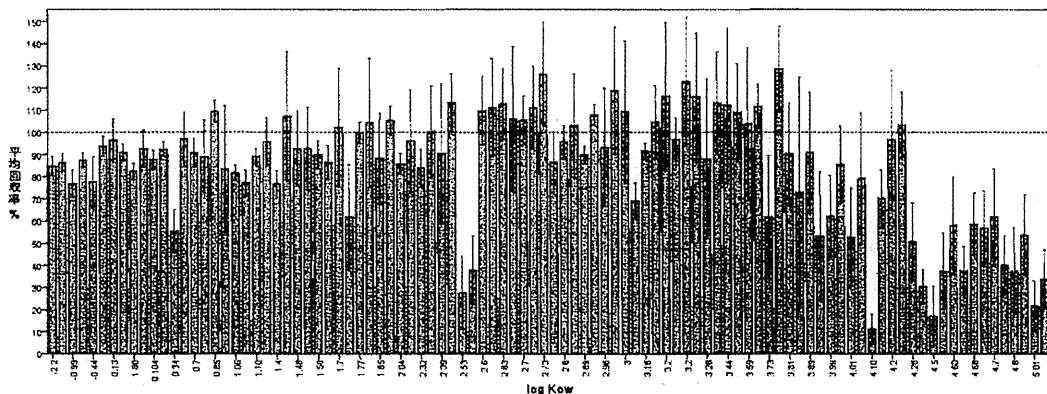


図4 難揮発性化学物質(横軸)の添加回収結果。バーは回収率の平均値の95%信頼区間を示す。

と濃度から調査地点の汚染の全体像や発生源を把握することができる。定量の精確さも一部の高極性物質を除けば、個別分析法と比べて若干劣るものの、環境分析には十分な精度を有している。

開発した半揮発性化学物質網羅分析法を用いて中国長江河口<sup>13)</sup>、天津市河川、ベトナムの主要2都市(ハノイ、ホーチミン)の河川<sup>14)</sup>、及び日本全国の中小11河川を調査した<sup>9)</sup>。長江は2013年3月に上海市河口域の9地点において表層と水深5mの河川水(18試料)を採水して分析した。天津市は、2013年12月に市内及び郊外の河川から採水した20試料を分析した。ハノイ(5試料)とホーチミン(11試料)は、2013年9月に市内河川(運河)と郊外の河川から採水して分析した。日本の河川は、農薬汚染を調査する目的で主に農業地帯を流れる11河川を対象に1995年の農薬使用時期(5月及び8月)に計150試料を採水して分析した。その結果の概要を表1に示す。また、各国での検出頻度上位10物質を表2に示す。全検出物質の合計濃度は、ベトナム>天津>>長江≧日本となった。ベトナムでは下水道や廃水処理施設が未整備であるため、また天津市も下水道が完全に整備されていないため、未処理の廃水や処理が不十分な廃水が河川を汚濁していることが確認された。長江の流量は年間1兆m<sup>3</sup>と膨大であるにもかかわらず、日本の河川とほぼ同じ物質数と濃度が検出された。これは、その流域の4億の人口、2,640万haの耕地、及び中国全体の40%を占める工業生産高から予想される大量の化学物質の排出が原因であろう。

高検出頻度物質に注目すると、長江は主に工業由来の化学物質によって汚染されていることが分かった。これは、長江流域に多数の工場が立地していることを反映していると考えられた。一方、天津市内の河川からは、ヒトの糞便マーカー物質、多環芳香族炭化水素、PPCPsが高頻度で検出された。この結果から、天津市内河川は生活廃水と石炭燃焼の影響を受けていると考えられた。ベトナムの河川からは、ヒト糞便、PPCPs、界面活性剤分解物などが高頻度かつ高濃度で検出されたため、生活廃水が処理されずに河川に流入していると考えられた。また、ハノイとホーチミンの中心部を流れる河川からピレスロイド系殺虫剤のPermethrin(ペルメトリン)が高

濃度(1.9~4.4 µg/L)で検出された。検出地点から考えて農業向けではなく、衛生目的での使用が原因と考えられる。日本ではPPCPsと農薬が高頻度に検出されたが、農繁期に採水したため農薬が検出され、下水道未整備地域ではPPCPsが検出されたと推察された。また、多くのPPCPsがベトナムと日本の両国で検出されており、両国では同様の製品が使用されていることが示唆された。

### 3.2 中国長江及びベトナム河川の難揮発性化学物質汚染

開発した難揮発性化学物質網羅分析法を用いて、半揮発性化学物質と同一地点で長江河口及びベトナム2都市の河川水を調査した。その結果の概要及び検出頻度上位10物質を表3と表4に示す。総検出濃度は、半揮発性物質と同様にベトナム河川が長江の約10倍であった。高頻度検出物質に関しては、6物質が両国の上位10物質に含まれ、これらが両国において大量に使用されていることが示唆された。抗生物質等の医薬品は、国にかかわらず同一環境媒体中の濃度がほぼ同一レベルであるといわれている<sup>15)</sup>が、ベトナムの濃度は長江の数倍から20倍であった。これは、発生源の影響を直接受ける市内河川と大河川の違いであろう。なお、高頻度検出農薬のTricyclazole(トリシクラゾール)、Diuron(ジウロン)、Fenobucarb(フェノブカルブ)は日本の水道原水からも高頻度に検出されている<sup>16)</sup>。さらに、高い頻度で検出されたPPCPsも2-Quinoxalinecarboxylic acid(2-キノキサリンカルボン酸)を除き日本を含む全世界で検出されており<sup>17), 18)</sup>、これらの物質が世界中の水環境中に存在していることを示している。2-Quinoxalinecarboxylic acidは、豚用の抗菌剤・成長促進剤であるCarbadox(カルバドックス)の代謝物であるが、発がん性のために多くの国で現在は使用が禁止されている。

ベトナムと長江では、雨季(豊水期)と乾季(渇水期)の2回調査を実施し、季節変動を調べた。その結果、雨季が乾季に比べて、検出物質数及び検出濃度がともに大きかった。また同様の傾向は、半揮発性化学物質についても確認された。化学物質の流入量が季節によらず同一ならば、河川流量が多い雨季の河川水中濃度が低くなると予想されるが、実際は

表1 中国長江河口、天津市、ベトナム2都市(ハノイ、ホーチミン)及び日本の中小河川の半揮発性化学物質調査結果概要。

項目	長江河口	天津市	ハノイ、ホーチミン	日本11河川
試料採取日、試料数	2013年3月、 18	2013年12月、 20	2013年9月、 15	2005年5月と8月、 150
検出物質数	39~81(66)	32~84(53)	52~77(66)	0~77(15)
総検出物質数	137	159	111	187
検出頻度10%以上の物質数	115	103	94	65
総検出濃度、µg/L	1.16~11.3(4.0)	6.8~164(20.1)	6.35~200(36)	0~819(3.1)

括弧は中央値

表 2 中国長江河口，天津市，ベトナム 2 都市（ハノイ，ホーチミン）及び日本の中小河川の半揮発性化学物質の検出頻度上位 10 物質。

No.	長江			天津				
	物質名	検出頻度， %	検出濃度， μg/L	用途・起源	物質名	検出頻度， %	検出濃度， μg/L	用途・起源
1	2(3H)-Benzothiazolone	100	0.158 - 1.39 (0.458)	医薬品， 農薬，染料， ポリマーの中間 原料	Coprostanol	95	ND - 5.33 (0.73)	人糞
2	Nitrobenzene	100	0.146 - 0.260 (0.225)	染料， 有機合成， 香料の中間原料	Caffeine	95	ND - 1.43 (0.28)	興奮薬
3	Aniline	100	0.091 - 0.250 (0.165)	染料， 有機合成， 香料の中間原料	Fluorene	95	ND - 0.29 (0.044)	多環芳香族 炭化水素
4	2-Nitroaniline	100	0.100 - 0.229 (0.172)	染料， 医薬品， 農薬中間原料	Phenanthrene	95	ND - 0.67 (0.017)	多環芳香族 炭化水素
5	Isoprothiolane	100	0.014 - 0.059 (0.028)	殺菌剤	Fluoranthene	90	ND - 0.23 (0.042)	多環芳香族 炭化水素
6	Bis(2-chloroisopropyl) ether	94	0.007 - 0.034 (0.018)	染料， 医薬品中間原料， 溶媒	Dibenzofuran	85	ND - 0.66 (0.049)	コールド 成分， 化学合成
7	2-Chloroaniline	89	0.004 - 0.020 (0.006)	染料， 医薬品， 農薬中間原料	Anthraquinone	85	ND - 0.29 (0.054)	染料の中間 原料
8	Paclobutrazol	83	0.010 - 0.033 (0.016)	植物成長調整剤	2-(Methylthio)- benzothiazole	85	ND - 31.8 (0.11)	加硫促進剤
9	2,6-Dichlorophenol	78	0.009 - 0.032 (0.020)	農薬等の中間原料	Epicoprostanol	80	ND - 1.57 (0.15)	人糞
10	2-(Methylthio)- benzothiazole	78	0.010 - 0.033 (0.018)	加硫促進剤	Anthracene	80	ND - 0.67 (0.14)	多環芳香族 炭化水素

No.	ベトナム			日本				
	物質名	検出頻度， %	検出濃度， μg/L	用途	物質名	検出頻度， %	検出濃度， μg/L	用途・起源
1	4-tert-Octylphenol	100	0.01 - 0.22 (0.03)	界面活性剤原料	L-Menthol	53	ND - 0.36 (0.072)	鎮痒薬
2	Ethanol, 2-phenoxy-	100	0.03 - 2.54 (0.13)	スキนครリーム， 溶剤	Bromobutide	53	ND - 2.93 (0.287)	除草剤
3	Diethyltoluamide	100	0.02 - 0.51 (0.12)	昆虫忌避剤	Caffeine	49	ND - 7.39 (1.38)	興奮薬
4	L-Menthol	100	0.01 - 11 (0.11)	鎮痒薬	Diethyltoluamide	48	ND - 0.609 (0.115)	昆虫忌避剤
5	Coprostanol	100	0.01 - 3 (5.2)	人糞	Squalane	45	ND - 1.77 (0.483)	化粧品
6	2-Ethyl-1-hexanol	94	ND - 2.2 (0.34)	可塑性原料， 皮膚軟化剤	Crotamiton	42	ND - 0.98 (0.302)	鎮痒薬
7	Benzyl alcohol	94	ND - 1.2 (0.41)	溶剤， 香料原料	Tributyl phosphate	41	ND - 0.16 (0.032)	難燃剤
8	Di(2-ethylhexyl) adipate	94	ND - 0.18 (0.09)	可塑性原料	Pyroquilon	38	ND - 1.66 (0.330)	殺菌剤
9	Caffeine	94	ND - 3.1 (0.21)	興奮薬	Molinate	37	ND - 0.31 (0.070)	除草剤
10	2,6-di-t-butyl-4-Methylphenol	88	ND - 0.41 (0.04)	酸化防止剤原料	Isophorone	35	ND - 0.088 (0.027)	溶剤

脂肪族炭化水素，フタル酸エステル及び人糞由来以外のステロール類を除く  
括弧は中央値(但し，日本は検出値の平均)

表3 中国長江河口及びベトナム2都市(ハノイ, ホーチミン)での難揮発性化学物質調査結果概要.

項目	長江河口	ハノイ, ホーチミン
試料採取日, 試料数	2013年3月, 18	2013年9月, 15
検出物質数	0-12(10)	7-33(16)
総検出物質数	12	51
検出頻度10%以上の物質数	12	43
総検出濃度, ng/L	210-340(272)	160-14,600(3,313)

括弧は中央値

表4 中国長江河口及びベトナム2都市(ハノイ, ホーチミン)での難揮発性化学物質の検出頻度上位10物質.

No.	長江			ベトナム				
	物質名	検出頻度, %	検出濃度, ng/L	用途	物質名	検出頻度, %	検出濃度, ng/L	用途
1	2-Quinoxalinecarboxylic acid	100	58-109 (79)	豚用抗菌性物質 Carbadoxの代謝物	2-Quinoxalinecarboxylic acid	100	19-515 (273)	豚用抗菌性物質 Carbadoxの代謝物
2	Tricyclazole	100	51-67 (58)	殺菌剤	Lidocaine	100	8-99 (46)	局所麻酔薬, 抗不整脈薬
3	Imidacloprid	100	22-51 (39)	殺虫剤	Dicyclohexylamine	94	9-565 (83)	化学製品中 間体
4	Carbendazim	100	17-33 (23)	防カビ剤 (殺菌剤)	Carbendazim	94	15-143 (87)	防カビ剤 (殺菌剤)
5	Cotinine	100	9-33 (12)	ニコチンの 代謝物	Cotinine	88	11-2,260 (290)	ニコチンの 代謝物
6	Bensulfuron-methyl	100	8-17 (13)	除草剤	Diuron	88	9-121 (53)	除草剤
7	Antipyrine	100	8-14 (11)	解熱鎮痛薬	Tricyclazole	81	16-531 (54)	殺菌剤
8	Thiamethoxam	89	8-28 (20)	殺虫剤	Fenobucarb	75	8-66 (23)	殺虫剤
9	Lincomycin	39	8-26 (9)	抗生物質	Lincomycin	69	85-3,550 (613)	抗生物質
10	Sulfamethoxazole	33	8-16 (12)	抗生物質	Sulfamethoxazole	63	27-1,100 (175)	抗生物質

括弧は中央値

逆であった。この理由としては、降雨によって土壌、道路及び建物などに蓄積していた化学物質が流出したことが一因と考えられる。このことから、化学物質による水環境汚染、特に水環境への流出量を調べるには、一般に行われている晴天時だけでなく雨天時の調査も重要であることが分かった。

以上の結果を総合すると、経済のグローバル化にともない近代的な生活や耕作法が全世界に広がって、同一・同種の化学製品や工業原料が全世界で使用されるようになり、汚染のグローバル化も進んでいることが確認された。

#### 4. まとめ

本研究から、同一の化学物質が国に関係なく広く検出されることが確認された。このような化学物質

による地球規模の汚染は二つのルートが考えられる。一つは大気や海流を介しての移動であり、もう一つは製品・原料や廃棄物の輸出入による移動である。大気や海流により汚染が拡大する物質は、POPsとしてストックホルム条約で規制されている。また、有害廃棄物の輸出入もバーゼル条約で規制されている。一方、製品や原料の輸出入による化学物質の移動は比較的自由であり、グローバル化にともない移動量も急増している。その結果、本文で示したように数多くの物質が日本、中国、ベトナムの環境を汚染することとなった。しかし、国により検出濃度は大きく異なっていた。日本では化学物質によるリスクに注意が払われ、適切に製造・使用・管理・廃棄が行われている。しかし、中国やベトナムでは日本ほどに注意が払われていないようである。化学物質への関心(啓蒙)を高めて適切に使用・管理・廃



棄することが、化学物質汚染の拡大を防ぎ、そのメリットを享受することにつながる。また、汚染の実態を把握してデータに基づいた対応をしていくことも重要であろう。そのためには、本文で紹介した網羅分析が有効なツールである。

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# Decomposition of 1,4-dioxane by vacuum ultraviolet irradiation: Study of economic feasibility and by-product formation



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## ABSTRACT

We report the first use of vacuum ultraviolet (VUV) treatment to decompose 1,4-dioxane, a persistent organic contaminant that is difficult to remove by conventional drinking water treatment processes. The efficiency of VUV treatment was compared to that of VUV- and UV-based advanced oxidation processes (AOPs) (VUV/TiO<sub>2</sub>, VUV/H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub>, and UV/H<sub>2</sub>O<sub>2</sub>), and by-product formation was investigated. VUV treatment decomposed 1,4-dioxane more rapidly than did UV and UV/TiO<sub>2</sub> treatments. The decomposition rate was enhanced when VUV irradiation was combined with TiO<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>. VUV/H<sub>2</sub>O<sub>2</sub> decomposed 1,4-dioxane more rapidly than UV/H<sub>2</sub>O<sub>2</sub> at a low H<sub>2</sub>O<sub>2</sub> dose (1 mg/L), but the rate difference became small at a high H<sub>2</sub>O<sub>2</sub> dose (5 mg/L). Electrical energy per order analysis revealed that VUV treatment, and the VUV- and UV-based AOPs, were economically feasible for 1,4-dioxane decomposition. Using raw water samples, we investigated by-product formation during VUV treatment and the effect of VUV irradiation on chlorinated disinfection by-product formation potential. Although the samples contained high concentrations of bromide, no bromate was produced by VUV treatment. VUV treatment slightly decreased trihalomethane formation potential (THMFP), whereas haloacetic acid formation potential (HAAFP) was unchanged, and total aldehyde concentration increased. The trend in HAAFP agreed with that had been reported for the VUV irradiation with much higher dose (Buchanan et al., 2006), whereas the trend in THMFP was different from that with much higher dose. THMFP, HAAFP, and aldehyde concentration were reduced by subsequent treatment with granular activated carbon (GAC) or biological activated carbon (BAC). Nitrite was produced by VUV treatment but disappeared after subsequent BAC treatment. These results suggest that VUV treatment should be combined with GAC or BAC treatment to suppress by-product formation.

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**Abbreviations:** 2-MIB, 2-methylisoborneol; AOP, advanced oxidation process; BAA, bromoacetic acid; BAC, biological activated carbon; BCAA, bromochloroacetic acid; BDCAA, bromodichloroacetic acid; BDCM, bromodichloromethane; CAA, chloroacetic acid; CDBP, chlorination disinfection by-products; CDBPFP, formation potential of CDBP; DBAA, dibromoacetic acid; DBCAA, dibromochloroacetic acid; DBCM, dibromochloromethane; DCAA, dichloroacetic acid; DTW, dechlorinated tap water; EE/O, amount of electrical energy required for 1 m<sup>3</sup> of contaminated water to bring about a reduction by one order of magnitude in target compound concentration; ES1, experimental setup 1; ES2, experimental setup 2; GAC, granular activated carbon; GC/MS, gas chromatograph/mass spectrometer; HAAFP, formation potential of HAAs; HAAs, haloacetic acids; JDWQS, Japanese drinking water quality standard; NOM, natural organic matter; SIM, selected ion monitoring; TBAA, tribromoacetic acid; TCAA, trichloroacetic acid; THMs, trihalomethanes; THMFP, formation potential of THMs; UV, ultraviolet; VUV, vacuum ultraviolet; VUVBP, VUV by-product; WHO, World Health Organization.

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## 1. Introduction

1,4-Dioxane, which is classified in Group 2B (possibly carcinogenic) by the International Agency for Research on Cancer, has been widely used as a stabilizing agent and solvent (Zenker et al., 2003) in chemical engineering applications, drug manufacturing, and the textile industry. In addition, 1,4-dioxane is present in many consumer products as a by-product of polyester synthesis (Black et al., 1983; Zenker et al., 2003), as well as in many household detergents and shampoos (Fuh et al., 2005; Tanabe and Kawata, 2008) as an impurity of surfactants (Guo and Brodowsky, 2000; Zenker et al., 2003). Industrial and domestic waste water contaminated with 1,4-dioxane flows into sewage treatment systems, where it is difficult to remove by means of conventional biological treatment processes (i.e., activated sludge treatment): no removal of 1,4-dioxane concentration was reported in a laboratory-scale experiment (Adams et al., 1994), and no or limited removal (0–30%) was observed in sewage treatment plants (Abe, 1999; Tanabe et al., 2006). Therefore, 1,4-dioxane is expected to be released into environmental waters after sewage treatment. In addition, 1,4-dioxane has been reported to be eluted from landfill sites and to contaminate leachates at concentrations of several to thousands of micrograms per liter, depending on the nature of the discarded materials (Isaacson et al., 2006; Lesage et al., 1990). Owing to its high hydrophilicity, 1,4-dioxane does not interact with soil particles and easily penetrates the ground (Zenker et al., 2003), which leads to contamination of groundwater rather than surface water.

The World Health Organization (WHO) has established guideline values for various chemical contaminants in drinking water (Guidelines for Drinking-water Quality), and the recommended value for 1,4-dioxane is  $<50 \mu\text{g/L}$ . However, 1,4-dioxane is difficult to remove from drinking water; it persists not only after conventional treatment consisting of coagulation, sedimentation, and sand filtration but also after activated carbon adsorption (McGuire et al., 1978). Oxidation processes such as ozonation (Adams et al., 1994) and chlorination (Klečka and Gonsior, 1986; McGuire et al., 1978) are also ineffective. Advanced oxidation processes (AOPs), such as a combination of ozone and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), have been reported to decompose 1,4-dioxane (Adams et al., 1994; Suh and Mohseni, 2004). In addition, ultraviolet (UV) irradiation in the presence of a photocatalyst may be another option (Coleman et al., 2007; Hill et al., 1997), but the powdered photocatalyst studied for this process is so fine (particle diameter, 20–25 nm) that the necessity of recovering the fine powder makes the process impractical.

AOP consisting of UV and  $\text{H}_2\text{O}_2$  has proven to be effective process for decomposition of organic contaminants, and has been already applied to full-scale drinking water treatment plants (Kruihof et al., 2007). In contrast, to our knowledge, vacuum ultraviolet (VUV) irradiation, which dissociates water molecules into hydroxyl radicals (Oppenländer and Sosnin, 2005), is a developing method that has not been applied to actual treatment plants, but is reported to be a powerful method for rapid decomposition of organic substances in water, including earthy-musty odor compounds (Kutschera et al., 2009), pharmaceuticals (Szabó et al., 2011), and pesticides (Imoberdorf and Mohseni, 2012). Moreover, the process is operationally simple and requires no chemicals that must be transported or stored. Therefore, it has the potential to be practical for use in urban water utilities that rely on a contaminated groundwater source for drinking water.

However, the nature of the reaction products and by-products formed from compounds of interest during VUV treatment must be considered, as is the case for other oxidation processes. During UV-based AOPs, 1,4-dioxane is reported to be transformed into various compounds, including 1,2-ethanediol monoformate (Stefan and Bolton, 1998), 1,2-ethanediol diformate (Maurino et al., 1997; Mehrvar et al., 2000; Stefan and Bolton, 1998), and methoxyacetic acid (Stefan and Bolton, 1998). These compounds are reportedly then transformed into acetic acid (Mehrvar et al., 2000) and formic acid (Mehrvar et al., 2000; Stefan and Bolton, 1998), which are eventually mineralized (Stefan and Bolton, 1998). In addition, during VUV treatment of raw water, by-products (VUVBPs) are formed from natural organic matter (NOM) present in the water, and some of these by-products may act as precursors of chlorination disinfection by-products (CDBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). CDBPs are toxic to humans (Hebert et al., 2010), and for some of them, guidelines and standards for their concentrations in drinking water have been established.

Detailed information about VUVBPs and VUVBP-derived CDBPs is limited. Buchanan et al. investigated changes in CDBP formation potential (CDBPFP) during VUV treatment and after treatment with biological activated carbon (BAC) and found that the THM and HAA formation potentials (THMFP and HAAFP, respectively) tend to decrease with VUV irradiation (Buchanan et al., 2006) and that THMFP and HAAFP tend to decrease further upon subsequent BAC treatment (Buchanan et al., 2008). However, because the main target of these investigators was NOM at markedly high concentrations (8–10 mg-DOC/L), VUV dose used in their studies were 16–186 J/cm<sup>2</sup>, which is several orders of magnitude higher than the doses required for the decomposition of persistent organic contaminants in raw water at trace levels (e.g., 0.1, 0.2, and 0.6 J/cm<sup>2</sup> for 2,4-dichlorophenoxyacetic acid (Imoberdorf and Mohseni, 2012), anatoxin-a (Afzal et al., 2010), and earthy-musty odor compounds (Kutschera et al., 2009)). The effect of low VUV doses on CDBPFP has not yet been investigated. The fact that THMFP initially increases upon  $\text{O}_3/\text{UV}$  treatment of surface water samples at a low UV dose and then decreases with increasing UV dose (Glaze et al., 1982) highlights the need for further research.

In the present study, we investigated the use of VUV treatment for 1,4-dioxane removal from water, paying particular attention to decomposition efficiency and by-product formation. In addition to VUV alone, we investigated VUV-based AOPs (VUV/ $\text{TiO}_2$  and VUV/ $\text{H}_2\text{O}_2$ ), UV-based AOPs (UV/ $\text{TiO}_2$  and UV/ $\text{H}_2\text{O}_2$ ), and UV alone, and we compared the performances of various treatments. For the VUV/ $\text{TiO}_2$  and UV/ $\text{TiO}_2$  treatments, we introduced a new photocatalyst consisting of  $\text{TiO}_2$  immobilized on a nonwoven fabric, which meant that no catalyst separation was required after the photocatalytic reactions. Furthermore, to investigate the economic feasibility of the treatments, we performed electric energy per order (EE/O) analysis of the decomposition of 1,4-dioxane. We also compared the removal of 1,4-dioxane with that of 2 earthy-musty odor compounds, 2-methylisoborneol (2-MIB) and geosmin, whose behaviors in AOPs have been well studied. For the second purpose, we used two natural water samples (a lake water sample and a groundwater sample) to investigate the formation of VUVBPs from NOM and inorganic ions at a VUV dose high enough for the decomposition of trace-level organic contaminants and to investigate CDBPFP. The target VUVBPs included 10 aldehydes, as well as nitrite and bromate; and the

**Table 1 – VUV and UV lamps used.**

	Energy consumption, W	Irradiation intensity measured at lamp surface, mW/cm <sup>2</sup>		Supplier
		185 nm	254 nm	
		VUV lamp 1	10	
UV lamp 1	10	0.0	11.1	Ube Industries, Ube, Japan
VUV lamp 2	65	20.8	50.9	Heraeus Noblelight, Hanau, Germany
UV lamp 2	65	0.0	50.2	Heraeus Noblelight, Hanau, Germany

target CDBPFP included 4 THMFPs and 9 HAAPFs. By-products derived from 1,4-dioxane were not measured individually, because the experiments were conducted at the very low 1,4-dioxane concentrations (50–100 µg/L) typically observed in contaminated groundwater (Abe, 1999), the by-product concentrations were expected to be well below their detection limits. Finally, we also investigated the effects of BAC and granular activated carbon (GAC) treatments on VUVBPs and CDBPFP.

## 2. Materials and methods

### 2.1. VUV and UV lamps

We used two types of low-pressure mercury vapor lamps, VUV and UV lamps, which differ in the glass materials that encapsulate the mercury vapor. The major resonance lines of a low-pressure mercury lamp are at 185 and 254 nm, but the glass of the UV lamps eliminates the 185-nm light (that is, VUV light). In contrast, the high-purity synthetic quartz glass of the VUV lamps transmits both wavelengths. Two sets of VUV and UV lamps with the same energy consumption values were prepared (Table 1); UV and VUV lamp sets 1 and 2 were used in combination with experimental setup 1 (ES1, Fig. 1) and experimental setup 2 (ES2, Fig. 2), respectively.

### 2.2. Photocatalyst

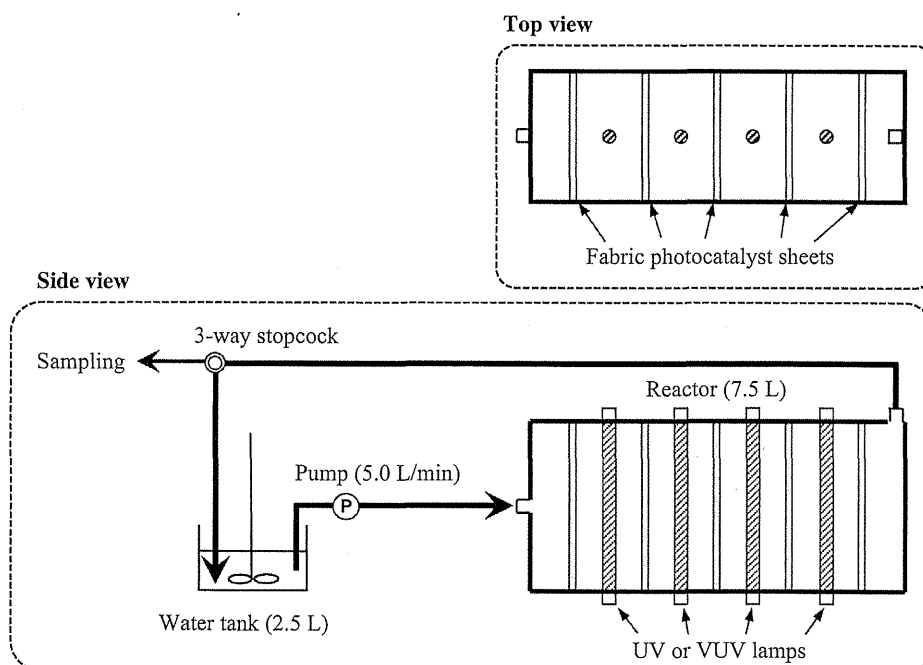
As a photocatalyst, we used a nonwoven fabric sheet made of amorphous SiO<sub>2</sub> fibers with an anatase TiO<sub>2</sub> surface layer

(crystalline size, ~8 nm) (Ishikawa et al., 2002); the fiber sheets were kindly supplied by Ube Industries (Tokyo, Japan). The effective area of each sheet was 96.7 cm<sup>2</sup>, and 5 sheets were installed in a photocatalytic reactor.

### 2.3. Water samples

Three types of water samples were used: buffered dechlorinated tap water (DTW), raw groundwater, and raw lake water (Table 2). To prepare the buffered DTW, we treated tap water (Hokkaido University, Sapporo, Japan) with an activated carbon cartridge (Toyo Roshi Kaisha) to eliminate free chlorine. Phosphate buffers with various pH values (5.5–8.0) were prepared by dissolving NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> (20 mmol/L) in DTW in various proportions. The phosphate buffers were spiked with 1,4-dioxane, 2-MIB, and geosmin at final concentrations of 50 µg/L, 100 ng/L, and 100 ng/L, respectively. Finally, the buffers were spiked with KBr at a concentration of 100 µg-Br/L. The buffered DTW was used mainly for investigating the effect of pH on 1,4-dioxane decomposition and the formation of bromide by-products.

The groundwater was withdrawn from a drinking water source from September to December 2012 in Tachikawa, Japan, and was stored at 4 °C until use. The groundwater was not spiked with 1,4-dioxane, because the water was already contaminated with 1,4-dioxane at a concentration of approximately 100 µg/L. H<sub>2</sub>O<sub>2</sub> was added to the groundwater at a dose of either 1 or 5 mg/L for investigation of the effects of added H<sub>2</sub>O<sub>2</sub> on the efficiencies of the VUV- and UV-based AOPs. The



**Fig. 1 – Experimental setup 1, photocatalysis reactor operated in circulation mode.**