

(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 C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub> 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

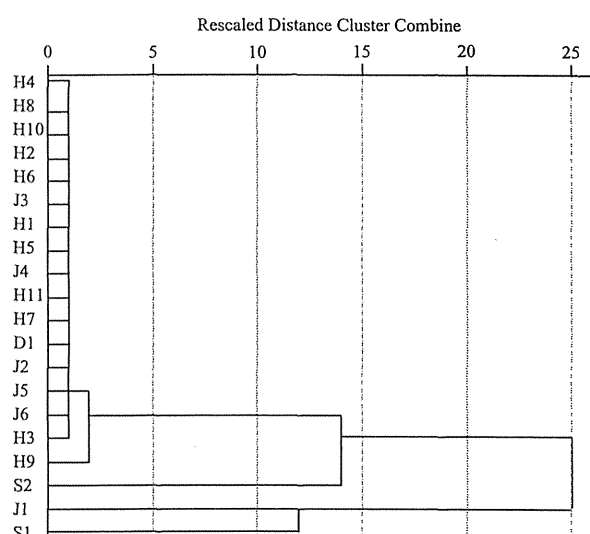


Fig. 2. Dendrogram of hierarchical cluster analysis with Ward's method and squared Euclidean distance for 20 sampling locations.

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.

### Acknowledgements

We are grateful to Dr. Graeme Allinson (University of Melbourne, Melbourne, Australia) and Dr. Mayumi Allinson (University of Melbourne, Melbourne, Australia) for their kind proofreading, useful comments, and constructive suggestions on this manuscript.

### 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>.

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

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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

受付：2014 年 4 月 16 日, 受理：2014 年 9 月 23 日

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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>51, 61</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>51, 61</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>51</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>71</sup>やStandard Methods for the Examination of Water and Wastewater<sup>81</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>91</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>101</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)

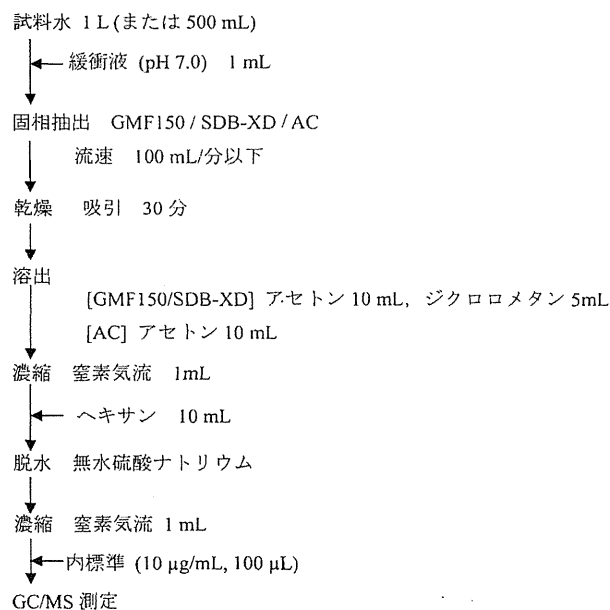


図1 半揮発性化学物質の網羅分析法フローチャート。

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Aquis 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

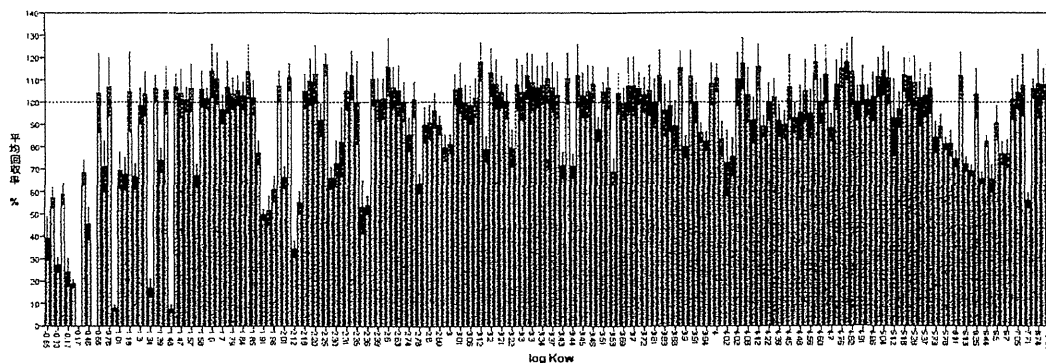


図2 半揮発性化学物質(横軸)の添加回収結果. バーは回収率の平均値の95%信頼区間を示す。

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。

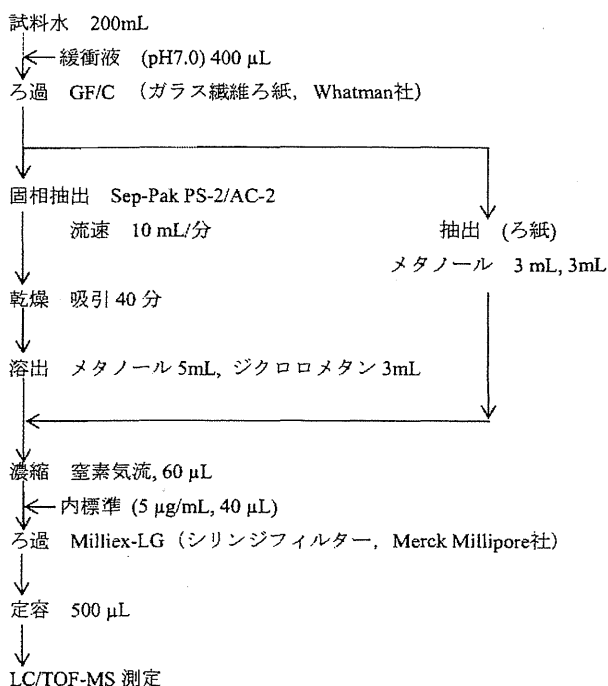


図3 難揮発性化学物質の網羅分析法フローチャート。

## 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

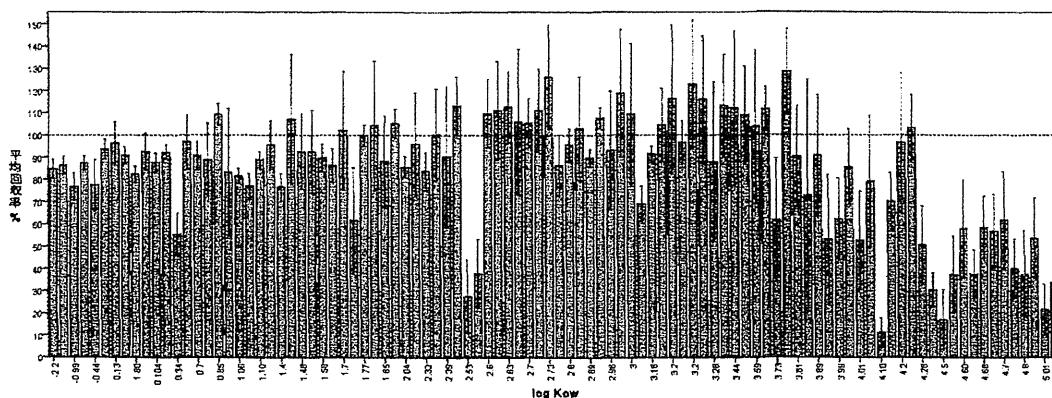


図4 難揮発性化学物質(横軸)の添加回収結果。バーは回収率の平均値の95%信頼区間を示す。



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と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)	コールター ル成分， 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
ベトナム				日本				
No.	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)	可塑剤原料， 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)	可塑剤	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。

## 謝 辞

長江調査は科研費(23404002)、ベトナム調査はJSPS(Japan Society for the Promotion Science, 日本学術振興会)-VAST(Vietnam Academy of Science and Technology, ベトナム科学アカデミー)二国間交流事業及び北九州市学術・研究振興事業調査研究助成金の支援を受けて実施した。記して感謝する。

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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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### ARTICLE INFO

#### Article history:

Received 30 September 2014

Received in revised form 14

November 2014

Accepted 26 November 2014

Available online 5 December 2014

#### Keywords:

Activated carbon adsorption

Chlorination disinfection

by-product

Haloacetic acid formation potential

Hydrogen peroxide

Photocatalyst

Trihalomethane formation potential

### 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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<http://dx.doi.org/10.1016/j.psep.2014.11.005>

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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 (Kruithof 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/TiO<sub>2</sub> and VUV/H<sub>2</sub>O<sub>2</sub>), UV-based AOPs (UV/TiO<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>), and UV alone, and we compared the performances of various treatments. For the VUV/TiO<sub>2</sub> and UV/TiO<sub>2</sub> treatments, we introduced a new photocatalyst consisting of TiO<sub>2</sub> 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	1.2	11.3	Ube Industries, Ube, Japan
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  $\mu\text{g/L}$ ) 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

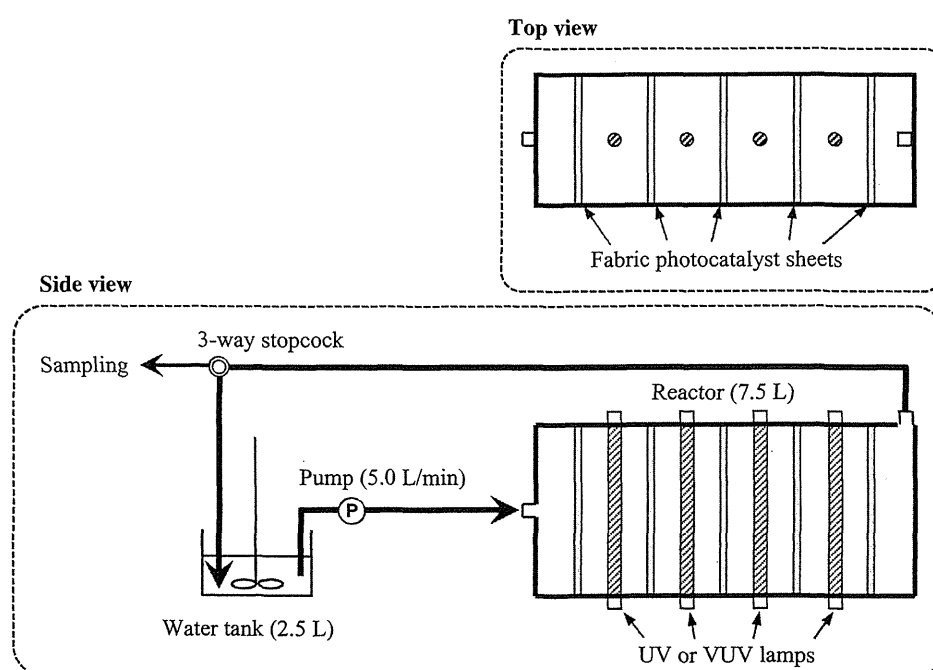
As a photocatalyst, we used a nonwoven fabric sheet made of amorphous  $\text{SiO}_2$  fibers with an anatase  $\text{TiO}_2$  surface layer

(crystalline size,  $\sim 8$  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  $\text{cm}^2$ , 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  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  (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  $\mu\text{g/L}$ , 100 ng/L, and 100 ng/L, respectively. Finally, the buffers were spiked with KBr at a concentration of 100  $\mu\text{g-Br/L}$ . 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  $\mu\text{g/L}$ .  $\text{H}_2\text{O}_2$  was added to the groundwater at a dose of either 1 or 5 mg/L for investigation of the effects of added  $\text{H}_2\text{O}_2$  on the efficiencies of the VUV- and UV-based AOPs. The



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

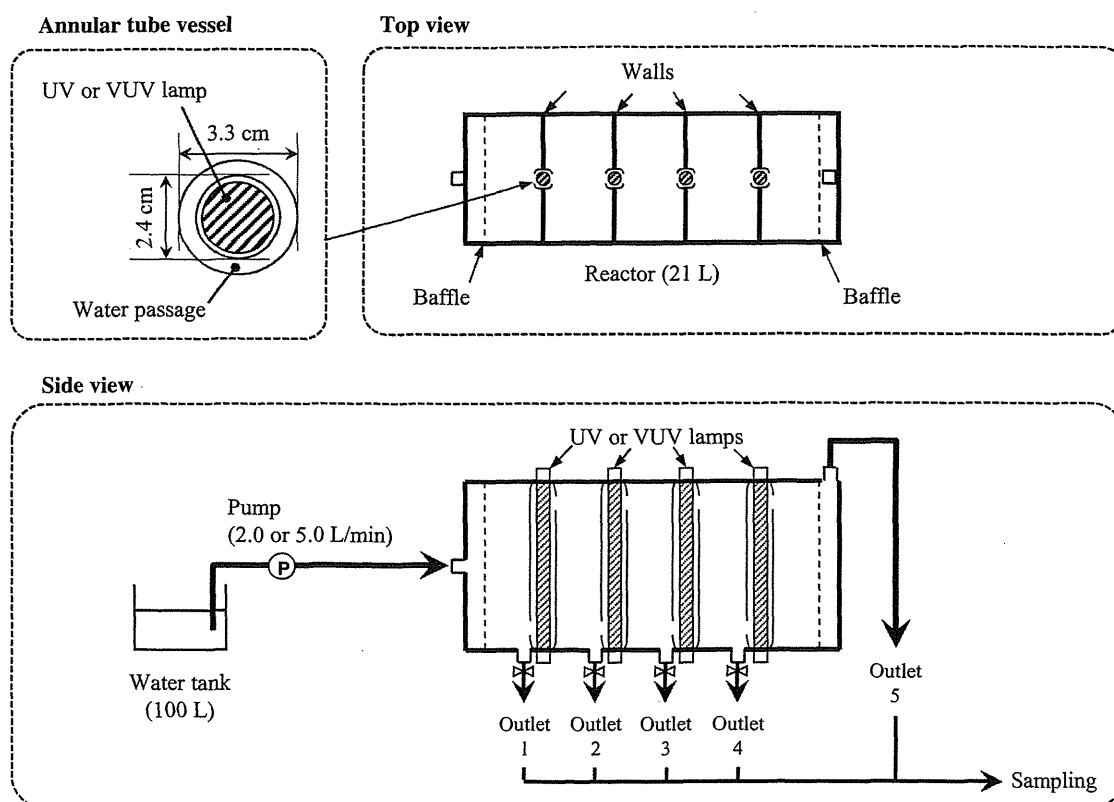


Fig. 2 – Experimental setup 2, photolysis reactor operated in one-pass mode.

groundwater was used mainly for feasibility studies: specifically, the decomposition of 1,4-dioxane, the effect of added  $\text{H}_2\text{O}_2$ , and by-product formation from NOM and nitrate were investigated with the groundwater.

The lake water was collected from Lake Hakucho (Tomakomai, Japan) on November 20, 2012, and was stored at 4 °C until use. The area upstream of the lake is covered with broad-leaved forest and swamp grassland, and therefore the lake water has a high proportion of NOM relative to anthropogenic organic matter. The lake water was filtered with a glass fiber filter ( $\phi = 0.5 \mu\text{m}$ , GB-140, Toyo Roshi Kaisha, Tokyo, Japan) to remove suspended solids prior to use in the experiments. The lake water was used to investigate by-product formation from NOM and nitrate.

Chemicals added to the water samples were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as supplied without further purification.

#### 2.4. Experimental setup 1

Decomposition of 1,4-dioxane, the effects of the  $\text{TiO}_2$  photocatalyst and pH, and bromate formation from bromide were investigated with ES1 (Fig. 1). ES1 consisted of a water tank, a pump, and a photocatalysis reactor (Aquasolution, Ube Industries, Tokyo, Japan) and was operated in circulation mode.

The volume of the reactor was 7.5 L. Four evenly spaced lamp inserts were located along the center line of the reactor, and either VUV lamp 1 or UV lamp 1, which had been turned on and allowed to warm up prior to the experiment, was installed in each insert. The reactor was equipped with five evenly spaced slots into which the fabric photocatalyst sheets were installed.

The water tank was charged with 10 L of buffered DTW, which was then pumped into the reactor at a constant flow rate of 5.0 L/min. The water passed through the photocatalyst sheets in the flow direction when the sheets were installed. The irradiated water then returned to the water tank, where it was completely mixed with a mechanical stirrer. Samples were periodically withdrawn from a three-way stopcock, and the concentrations of 1,4-dioxane, 2-MIB, and geosmin in the samples were measured.

Overall irradiation time ( $T$ , min) in the continuous decomposition experiments conducted in circulation mode was calculated as follows:

$$T = \frac{V_t}{V} \cdot t \quad (1)$$

where  $t$  is the sampling time (min),  $V_t$  is the volume of the water at sampling time  $t$  (L), and  $V$  is the volume of the reactor (L).

Table 2 – Water samples used.

	DOC mg/L	OD260 $\text{cm}^{-1}$	Turbidity NTU	pH
Buffered dechlorinated tap water	0.7	0.003	0	5.5–8.0
Groundwater	0.2	0.001	0	7.8
Lake water	2.6	0.098	8.1	7.6



For comparison of the results obtained with the two different ESs, the apparent decomposition rate constants ( $k$ ) were standardized by the electric power consumption of the VUV or UV lamps:  $k$  values were determined from the slopes of plots of  $\ln(C_T/C_0)$  versus the electric power consumption of the system per unit volume of water ( $E$ , J/L) (Eq. (2)):

$$\ln \frac{C_T}{C_0} = -kE \quad (2)$$

where  $C_T$  is the concentration of the target compound at overall irradiation time  $T$  and  $C_0$  is the initial concentration of the target compound.  $E$  was calculated as follows:

$$E = \frac{nP}{V} \cdot 60T \quad (3)$$

where  $n$  is the number of lamps (dimensionless), and  $P$  is the electric power per lamp (W).

## 2.5. Experimental setup 2

The effect of  $H_2O_2$  on 1,4-dioxane removal, aldehyde formation from NOM, and nitrite formation from nitrate were investigated with ES2 (Fig. 2). ES2 consisted of a water tank, a pump, and a photolysis reactor (Aquasolution, Ube Industries) and was operated in one-pass mode. The water tank was charged with groundwater (100L), which was then pumped into the reactor at a constant flow rate of 5.0L/min. To enhance the efficiency of VUV irradiation, we used a reactor that differed from that used for ES1 as follows. The reactor (volume, 21L) was vertically divided into five equal-volume chambers by walls equipped with annular tube vessels through which the water had to pass to flow to the next chamber. The vessels were made of quartz silica that transmitted both UV and VUV light. The internal and external diameters of the vessels were 2.4 and 3.3 cm, respectively. Lamps, either VUV lamp 2 or UV lamp 2, that had been turned on and allowed to warm up prior to the experiment were inserted in the internal wall of the vessels. The water passed between the internal and external walls from the bottom to the top, and then to the next chamber: thus, the water was forced to flow in close proximity to the lamps. Because water molecules readily absorb VUV light, hydroxyl radicals are generated only in a very thin water layer close to the lamp surface (i.e., just outside the lamp sleeve). Moreover, because the diffusion coefficient of hydroxyl radicals is  $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$  (LaVerne, 1989) and its lifetime in water is short ( $10^{-9}$ – $10^{-6}$  s (LaVerne, 1989)), the hydroxyl radicals were expected to be involved in reactions only in the immediate vicinity of where they were generated (i.e., only around the lamp sleeve). Finally, the treated water was discharged from outlet 5. Samples were withdrawn from outlets 1–5, and the concentrations of 1,4-dioxane in the samples were measured. Dividing the concentrations of 1,4-dioxane in the samples from outlets 1–5 by the concentration in the samples from outlet 1 gave the residual ratios.

Decomposition rate constants were determined as described in Section 2.4: that is,  $k$  values were determined from the slopes of plots of  $\ln(C_T/C_0)$  versus  $E$  (Eq. (2)).  $E$  (J/L) was calculated as follows:

$$E = 60 \cdot \frac{nP}{v} \quad (4)$$

where  $n$  is the number of lamps by which the raw water had been irradiated ( $n=1, 2, 3,$  and  $4$  for outlets 2, 3, 4, and 5, respectively), and  $v$  is the flow rate of the raw water (L/min).

## 2.6. By-product formation and its control by GAC treatment

VUVBPs and CDBPFP were investigated with ES2. The water tank was charged with either lake water or groundwater (100L), which was then pumped into the reactor at a constant flow rate of 2.0L/min in one-pass mode. The VUV-treated water was collected from outlet 5. In a preliminary experiment, we confirmed that the experimental conditions, including the VUV dose, were sufficient to remove 1,4-dioxane: specifically, the 1,4-dioxane concentration in the groundwater dropped from approximately 100  $\mu\text{g/L}$  to less than 10  $\mu\text{g/L}$ , which is lower than the WHO drinking water guideline (50  $\mu\text{g/L}$ ) and the Japan regulation value (50  $\mu\text{g/L}$ ). Under these conditions, the electric power consumption rate was calculated to be 7.8 kJ/L, which was much lower than the rates reported by Buchanan et al. (2006) ( $3.2 \times 10^2$ – $3.7 \times 10^3$  kJ/L) whose main target was high concentration of NOM.

To investigate GAC adsorption of the VUVBPs, we used two types of GAC: a virgin GAC and a used GAC. The virgin GAC (coal-based GAC, LG-20S, Swing Corp., Tokyo, Japan) was washed thoroughly with Milli-Q water to remove impurities and then dried in an oven at 103°C overnight, cooled to room temperature, and stored in a desiccator until use. The used GAC was a coal-based GAC (Shanxi Xinhua Protective Equipment, Taiyuan, China) that had been in service for 6 years in a full-scale drinking water treatment plant in Tokyo and had been collected when the GAC bed was replaced. This spent adsorbent, which might possess biological activity, was expected to act as BAC (hereafter, BAC). The BAC was washed thoroughly with Milli-Q water to remove impurities. Either BAC or virgin GAC was packed to a bed depth of 100 cm in an acrylic column with an internal diameter of 1.5 cm. The VUV-treated water was fed into BAC and GAC columns at a constant flow rate of 16 mL/min (10 min of contact time) by peristaltic pumps. The column effluent was collected on days 11 and 12 of operation. VUVBPs and the CDBPFP were almost the same in the samples withdrawn on two days. 1,4-Dioxane remaining in the VUV-treated water completely broke through the virgin GAC bed by day 11 of operation. Therefore, samples were collected after the GAC bed was pseudo-stabilized. On the other hand, the BAC column had been already broken through in terms of 1,4-dioxane at the beginning of the filtration. The data provided in Section 3 are averages of the concentrations in the samples collected on days 11 and 12.

To determine CDBPFP, we supplemented aliquots of raw water, VUV-treated water, and VUV/GAC-treated water with sodium hypochlorite (Asahi Glass Co., Tokyo, Japan) in an amount sufficient to result in a residual free chlorine concentration of 1–2 mg- $\text{Cl}_2/\text{L}$  after 24 h. The vessels containing the chlorinating water samples were tightly sealed to prevent vaporization of chlorine and the by-products and were incubated in the dark at 20°C for 24 h.

## 2.7. Quantification methods

Concentrations of 1,4-dioxane, 2-MIB, and geosmin were measured by gas chromatography/mass spectrometry (GC/MS) on a QP2010 Plus instrument (Shimadzu Co., Kyoto, Japan) coupled to a purge-and-trap pretreatment system (Aqua PT 5000)

Plus, AQUAauto 70, GL Science Inc., Tokyo, Japan) and a capillary column (length, 30 m; i.d., 250  $\mu\text{m}$ ; thickness, 0.25  $\mu\text{m}$ ; HP-5 ms, Agilent Technologies, Palo Alto, CA, USA). GC/MS was performed in selected ion monitoring (SIM) mode with geosmin- $d_3$  and 1,4-dioxane- $d_8$  as internal standards. The detected fragment ions ( $m/z$ ) of the compounds were as follows: 1,4-dioxane, 88; 2-MIB, 95; geosmin, 112; 1,4-dioxane- $d_8$ , 96; geosmin- $d_3$ , 115.

Bromoform, dibromochloromethane (DBCM), bromodichloromethane (BDCM), and chloroform in the chlorinated waters were quantified by GC/MS (QP2010 Plus) with a purge-and-trap sample concentrator (AQUA PT 5000J Plus). A capillary column (length, 60 m; i.d., 250  $\mu\text{m}$ ; thickness, 0.25  $\mu\text{m}$ ; InertCap AQUATIC, GL Sciences) was used for sample separation. GC/MS was performed in SIM mode.

Nine HAAs (bromoacetic acid (BAA), chloroacetic acid (CAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA), dibromochloroacetic acid (DBCBA), bromodichloroacetic acid (BDCBA), and trichloroacetic acid (TCAA)) were extracted from the chlorinated waters by a liquid–liquid extraction method with methyl tert-butyl ether, derivatized with *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine according to Standard Methods for the Examination of Water (JWWA, 2011), and quantified by GC/MS (7890A GC/5975C MS, Agilent Technologies). A capillary column (length, 30 m; i.d., 250  $\mu\text{m}$ ; thickness, 1.0  $\mu\text{m}$ ; DB-5MS, Agilent Technologies) was used for sample separation. GC/MS was performed in SIM mode.

Ten aldehydes (formaldehyde, propanal, butanal, pentanal, hexanal, heptanal, octanal, nonanal, benzaldehyde, and glyoxal) and 1,4-dioxane were quantified by GC/MS (QP2010 Plus) with a purge-and-trap sample concentrator (AQUA PT 5000J Plus). A capillary column (InertCap AQUATIC) was used for sample separation. GC/MS was performed in SIM mode. Because acetaldehyde could not be quantified reproducibly, it was not considered in the present study; it was detected in some samples, possibly as a result of contamination from the acrylic column used or from the atmosphere.

Bromate concentration was measured with a high-performance liquid chromatograph combined with an electrospray ionization tandem mass spectrometer (API3000, AB Sciex Instruments, Foster City, CA, USA) or a hybrid quadrupole-orbitrap mass spectrometer (Q Exactive, Thermo Fisher Scientific Inc., Waltham, MA, USA). Bromide, nitrate, and nitrite concentrations were measured with an ion chromatograph (DX-120, Dionex, Sunnyvale, CA, USA) equipped with a separation column (IonPac AS14, Dionex).

### 3. Results and discussion

#### 3.1. Decomposition of 1,4-dioxane by VUV treatment and effect of $\text{TiO}_2$ on the decomposition

We evaluated the changes in the residual ratios of 1,4-dioxane, 2-MIB, and geosmin at pH 7.0 with ES1 (Fig. 3). No decrease in the residual ratios was observed in the control experiments (no photocatalyst in the dark, gray diamonds), which implies that adsorption on the apparatus and evaporation were negligibly small. Under UV irradiation (gray triangles), the residual ratios for all the target compounds decreased, but only slightly, indicating that the extent of direct UV photolysis was limited. Slight reductions in the amounts of 2-MIB and geosmin under

UV irradiation have been reported previously (Kutschera et al., 2009; Rosenfeldt et al., 2005), in agreement with our observations.

UV irradiation with the photocatalyst (white triangles) increased the decomposition of the target compounds relative to that in the absence of the photocatalyst. Decomposition of 1,4-dioxane by irradiation with xenon lamps (Maurino et al., 1997) and low-pressure mercury vapor fluorescent lamps (Mehrvan et al., 2002) has been reported to be improved by the addition of  $\text{TiO}_2$ , which agrees with our results. Rapid degradation of 2-MIB and geosmin by UV/ $\text{TiO}_2$  treatment has also been reported (Lawton et al., 2003), which also agrees with our results.

UV irradiation of water in the presence of a  $\text{TiO}_2$  photocatalyst generates positive holes ( $h^+$ ) and hydroxyl radicals ( $^{\bullet}\text{OH}$ ) (Gaya and Abdullah, 2008),



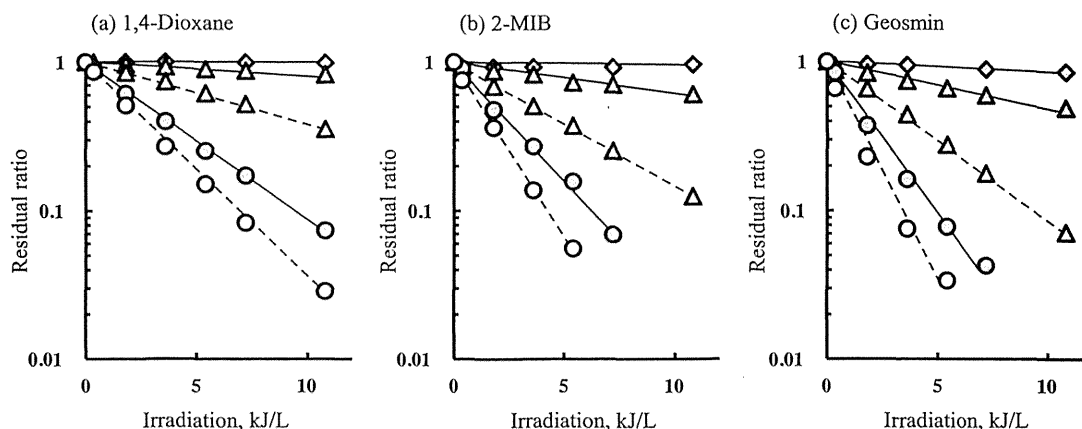
which are expected to play important roles in the decomposition of organic compounds. Additionally, direct photolysis at 254 nm is also expected to contribute to their decomposition. Klečka and Gonsior (1986) reported that 1,4-dioxane is decomposed by Fenton's reaction, during which hydroxyl radicals play a key role. In our system, 1,4-dioxane may have been decomposed mainly by the hydroxyl radicals generated by UV irradiation of the photocatalyst.

All three compounds were effectively decomposed by VUV irradiation (gray circles). To our knowledge, this is the first report of the use of VUV irradiation of water to remove 1,4-dioxane, which is one of the most persistent organic compounds (Zenker et al., 2003). Even though the electric power of the VUV lamps was the same as that of the UV lamps, the target compounds were decomposed to a greater extent with the former than with the latter. Moreover, the extent of decomposition with the VUV lamps in the absence of the photocatalyst was greater than that with the UV lamps in the presence of the photocatalyst. When water is irradiated with the VUV lamps, direct photolysis at 254 nm is expected to be accompanied by water homolysis: irradiation at 185 nm on water has been reported to result in homolysis and hydroxyl radical production (Oppenländer, 2007):



Zoschke et al. (2014) reported that these two mechanisms, direct photolysis and decomposition by hydroxyl radicals, are the main contributors to the decomposition of contaminants in water upon VUV irradiation. However, in the present study, the fact that the extent of direct UV photolysis was limited and that decomposition of the target compounds was greatly improved by VUV irradiation indicates that hydroxyl radicals generated by water homolysis effectively decomposed the target compounds. Kutschera et al. (2009) have reported that decomposition of 2-MIB and geosmin during VUV irradiation is dominated by the radical reaction.

VUV irradiation in the presence of the photocatalyst (white circles) greatly enhanced the decomposition of the target compounds. The enhancement was most likely not due to a photocatalytic reaction caused by VUV light. Water molecules readily absorb VUV light; the absorption coefficient of water for VUV light ( $\lambda = 184.9 \text{ nm}$ ) is reported to be  $1.80 \pm 0.01 \text{ cm}^{-1}$  at



**Fig. 3** – Changes in residual ratios of (a) 1,4-dioxane, (b) 2-methylisoborneol (2-MIB), and (c) geosmin during VUV (circles) and UV (triangles) irradiation at pH 7.0 (experimental setup 1, 40 W, circulation mode) in the absence (gray) or presence (white) of photocatalyst. The gray diamonds indicate data for control experiments without photocatalyst in the dark.

20 °C (Weeks and Gordon, 1963). Because the distance between the VUV lamp and the photocatalyst sheet was 3.5 cm in our experimental configuration, the irradiation intensity at the surface of the photocatalyst sheet was quite small, calculated to be at most <0.2% of the irradiation intensity at the surface of the lamp slot. In contrast, the UV absorption coefficient of the raw water used in the present study was measured to be  $0.001 \text{ cm}^{-1}$  at 254 nm, indicating that unlike VUV light, UV light was not absorbed by the water molecules and thus the photocatalyst received UV light and was excited. Therefore, the decomposition enhancement was most likely due to a UV photocatalytic reaction. The extent of enhancement due to the photocatalyst sheets was smaller for VUV treatment than for UV treatment because the amount of hydroxyl radicals generated by water homolysis upon VUV irradiation was most likely very large compared to the amount generated by photocatalysis.

To compare the efficiencies of the AOPs for 1,4-dioxane decomposition, we calculated EE/O values, that is, the amount of electric energy required to reduce the concentration of a target compound in  $1 \text{ m}^3$  of contaminated water by one order of magnitude (Bolton James et al., 2001). EE/O has been used to directly compare treatment AOP-based technologies (Zoschke et al., 2012). EE/O values were calculated as follows (batch operation) (Bolton James et al., 2001):

$$\text{EE/O} = \frac{P \cdot t}{V \cdot \log(c_0/c)} \quad (8)$$

where  $P$  is electric power (kW),  $t$  is time (h),  $V$  is reactor volume ( $\text{m}^3$ ),  $c$  is 1,4-dioxane concentration at time  $t$ , and  $c_0$  is initial 1,4-dioxane concentration. The EE/O values decreased in the order  $\text{UV} > \text{UV/TiO}_2 > \text{VUV} > \text{VUV/TiO}_2$  (Table 3). Systems are considered to be economically feasible when the EE/O value is less than 10 (Andrews et al., 1995). On the basis of this criterion,

**Table 3** – Decomposition rate constants ( $k$ ) and EE/O values for 90% decomposition of 1,4-dioxane in buffered dechlorinated tap water.

	$k$ , L/kJ	EE/O, kWh/( $\text{m}^3$ order)
UV	0.057	11
UV/TiO <sub>2</sub>	0.29	2.2
VUV	0.77	0.83
VUV/TiO <sub>2</sub>	1.1	0.58

VUV, VUV/TiO<sub>2</sub>, and UV/TiO<sub>2</sub> treatments are economically feasible for 1,4-dioxane decomposition, whereas UV treatment is not. However, because the cost of the photocatalyst sheets was not taken into account in the EE/O calculations, the actual EE/O values for VUV/TiO<sub>2</sub> and UV/TiO<sub>2</sub> treatments would be larger than the values shown in Table 3.

In the present study, 2-MIB decomposed to a lesser extent than geosmin during VUV and UV irradiation both in the presence and absence of the photocatalyst. The same tendency has previously been reported for VUV irradiation (Kutschera et al., 2009; Zoschke et al., 2012). The lower decomposition rates of 2-MIB during VUV, VUV/TiO<sub>2</sub>, and UV/TiO<sub>2</sub> treatment were most likely due to the fact that the rate constant for decomposition of 2-MIB by hydroxyl radicals is smaller than that for decomposition of geosmin (Glaze et al., 1990). 1,4-Dioxane decomposed to a lesser extent than did 2-MIB and geosmin in all of the treatments tested in the present study.

### 3.2. Effect of pH on decomposition of 1,4-dioxane

We also investigated the effect of pH on the decomposition rate constants of the target compounds (Fig. 4). The rate constants for the UV/TiO<sub>2</sub> process did not change substantially with pH (white triangles), whereas the rate constants for the VUV (gray circles) and VUV/TiO<sub>2</sub> (white circles) processes showed a relatively large dependence on pH. For all three compounds, the decomposition rate constants were largest at pH 5.5–6.0 and clearly decreased with increasing pH. The decomposition rate constants at pH 5.5–6.0 were roughly twice those at pH 7.5–8.0, indicating that maintaining a pH in the weakly acidic range would facilitate decomposition of these compounds.

VUV irradiation of water results in homolysis and production of hydroxyl radicals (Eq. (7)), which recombine to form H<sub>2</sub>O<sub>2</sub> (Oppenländer, 2007):



When H<sub>2</sub>O<sub>2</sub> absorbs UV light, hydroxyl radicals are generated by photolysis of the peroxidic bond (Lopez et al., 2003):



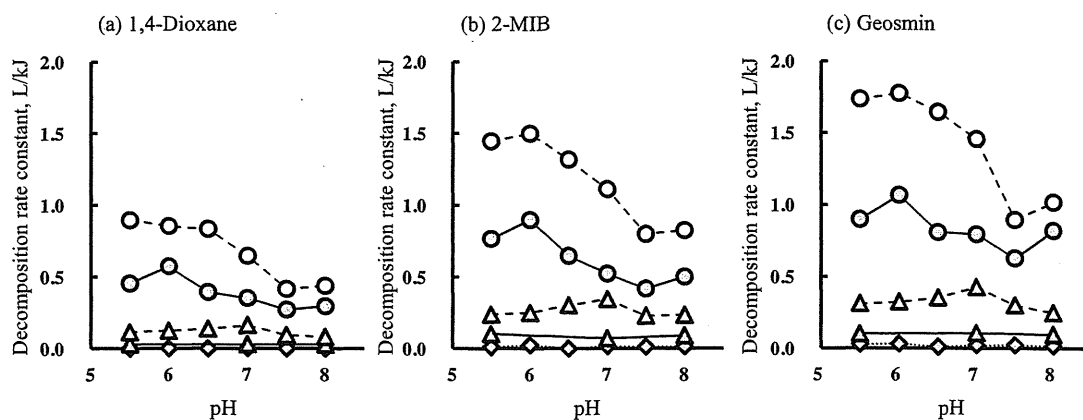


Fig. 4 – Effect of pH on rate constants for decomposition of (a) 1,4-dioxane, (b) 2-methylisoborneol (2-MIB), and (c) geosmin during VUV (circles) and UV (triangles) irradiation (experimental setup 1, 40 W, circulation mode) in the absence (gray) and presence (white) of the photocatalyst. The gray diamonds indicate data for control experiments without photocatalyst in the dark.

Accordingly, under UV light irradiation, hydroxyl radicals and  $\text{H}_2\text{O}_2$  are in equilibrium:



$\text{H}_2\text{O}_2$  is also in equilibrium with protons and  $\text{HO}_2^-$  anions (Joyner, 1912):



High  $\text{H}^+$  concentrations (low pH) drive the equilibrium toward the formation of  $\text{H}_2\text{O}_2$ , and its concentration increases accordingly. In turn, increases in the  $\text{H}_2\text{O}_2$  concentration drive the reaction shown in Eq. (11) toward the formation of hydroxyl radicals. These equilibrium considerations may explain why the decomposition rate constants were higher in the acidic pH range than in the basic pH range.

Alternatively, equilibrium of carbonate may have an influence on the pH-dependence of the decompositions. Carbonate acid, bicarbonate ion and carbonate ion dominate in the equilibrium roughly at low pH ( $\text{pH} < 6$ ), neutral to weak basic pH ( $6 < \text{pH} < 10$ ) and basic pH ( $\text{pH} > 10$ ), respectively. These carbonate species have reportedly scavenging ability of hydroxyl radicals that play a key role during the VUV irradiation, but the extents of the scavenging ability are different and in the order of carbonate acid  $\ll$  bicarbonate ion  $<$  carbonate ion (Liao and Gurol, 1995). Accordingly, the equilibrium of carbonate may explain why the decomposition rate constants were higher in the acidic pH range than in the basic pH range.

### 3.3. Effect of added $\text{H}_2\text{O}_2$ on decomposition of 1,4-dioxane.

Before investigating the effect of added  $\text{H}_2\text{O}_2$ , we evaluated the effect of system configuration by comparing the efficiencies of 1,4-dioxane decomposition using ES1 and ES2 with the same raw water (DTW that was withdrawn on the same day and then spiked with 1,4-dioxane) in the same operation mode (the one-pass mode) at the same flow rate (5.0 L/min). The rate constants for 1,4-dioxane decomposition were calculated to be 0.45 and 2.1 L/kJ for ES1 and ES2 ( $\text{EE}/\text{O} = 1.4$  and  $0.31 \text{ kWh}/(\text{m}^3 \text{ order})$ ), respectively; that is, the rate constant for ES2 was approximately 4.5 times that of ES1. Forcing the water to flow in the vicinity of the VUV lamps greatly enhanced

the decomposition rate of 1,4-dioxane, indicating that the system configuration is quite important for the design of VUV irradiation setups.

VUV treatment of groundwater in the absence of  $\text{H}_2\text{O}_2$  (Fig. 5, gray diamonds) decomposed the 1,4-dioxane in the water, and the apparent decomposition rate constant was calculated to be 0.75 L/kJ. This value was much smaller than that in DTW (2.1 L/kJ). Coexisting inorganic and organic materials have been reported to separately affect the decomposition rates of organic pollutants during VUV irradiation; for instance, carbonate and bicarbonate ions reportedly reduce decomposition rates (Imoberdorf and Mohseni, 2012; Kutschera et al., 2009). In our system, the bicarbonate concentration in the groundwater (13.3 mg/L) was much higher than that in the DTW (4.1 mg/L), which likely contributed to suppression of the decomposition rate in the groundwater relative to that in the DTW. Other coexisting materials may have influenced the 1,4-dioxane decomposition in the groundwater; further study of this issue is needed.

Addition of a 1 mg/L dose of  $\text{H}_2\text{O}_2$  to the VUV system enhanced the decomposition of 1,4-dioxane (Fig. 5, gray triangles): the decomposition rate constant increased by

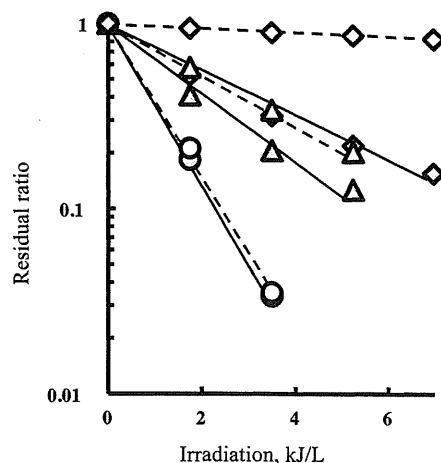


Fig. 5 – Effect of  $\text{H}_2\text{O}_2$  concentration on 1,4-dioxane decomposition during VUV (circles) and UV (triangles) irradiation (experimental setup 2, 240 W). Diamonds, triangles, and circles indicate data for  $\text{H}_2\text{O}_2$  concentrations of 0, 1, and 5 mg/L, respectively.

**Table 4 – Decomposition rate constants (*k*) and EE/O for 90% decomposition of 1,4-dioxane in groundwater.**

	<i>k</i> , L/kJ	EE/O, kWh/(m <sup>3</sup> order)
VUV	0.75	0.85
VUV + 1 mg/L H <sub>2</sub> O <sub>2</sub>	1.1	0.58
VUV + 5 mg/L H <sub>2</sub> O <sub>2</sub>	2.7	0.29
UV + 1 mg/L H <sub>2</sub> O <sub>2</sub>	0.85	0.76
UV + 5 mg/L H <sub>2</sub> O <sub>2</sub>	2.7	0.29

approximately 50%. When the dose of H<sub>2</sub>O<sub>2</sub> was increased to 5 mg/L (gray circles), 1,4-dioxane decomposition was accelerated even further: the decomposition rate constant increased to 3.6 times that in the absence of H<sub>2</sub>O<sub>2</sub>. As mentioned previously, H<sub>2</sub>O<sub>2</sub> absorbs VUV and UV light to produce hydroxyl radicals (Eq. (10)), which likely brought about the enhancement in the 1,4-dioxane decomposition.

Although the extent of decomposition of 1,4-dioxane by the UV treatment was quite limited in the absence of H<sub>2</sub>O<sub>2</sub> (white diamonds), adding a 1 mg/L dose of H<sub>2</sub>O<sub>2</sub> increased the extent of decomposition (white triangles). The decomposition rate constant for UV irradiation with a 1 mg/L dose of H<sub>2</sub>O<sub>2</sub> was smaller than that for VUV irradiation with the same H<sub>2</sub>O<sub>2</sub> dose but slightly larger than that for VUV treatment alone. When the H<sub>2</sub>O<sub>2</sub> dose was increased to 5 mg/L, the UV system effectively decomposed 1,4-dioxane (white circles): the decomposition rate constant was almost the same as that for VUV irradiation with a 5 mg/L dose of H<sub>2</sub>O<sub>2</sub>. At the lower H<sub>2</sub>O<sub>2</sub> dose, VUV/H<sub>2</sub>O<sub>2</sub> treatment was more effective than UV/H<sub>2</sub>O<sub>2</sub> treatment. However, as the H<sub>2</sub>O<sub>2</sub> dose was increased, the difference between the two treatments became negligibly small. At the higher dose of H<sub>2</sub>O<sub>2</sub>, the amount of hydroxyl radicals generated from the added H<sub>2</sub>O<sub>2</sub> (Eq. (5)) most likely became so large that the amount of hydroxyl radicals generated by VUV irradiation of the water molecules (Eq. (3)) became negligibly small.

For the feasibility study, we calculated EE/O values for flow-through operation as follows (Bolton James et al., 2001):

$$EE/O = \frac{P}{F \cdot \log(c_0/c)} \quad (13)$$

where *F* is flow rate (m<sup>3</sup>/h). H<sub>2</sub>O<sub>2</sub> was regarded as containing stored electric energy, which was added to the EE/O value: specifically, the calculation was conducted on the assumption that 1 kg of H<sub>2</sub>O<sub>2</sub> was equivalent to 10 kWh (Müller and Jekel, 2001). The EE/O value decreased when H<sub>2</sub>O<sub>2</sub> was added and continued to decrease as the H<sub>2</sub>O<sub>2</sub> dose was increased (Table 4): VUV > VUV/H<sub>2</sub>O<sub>2</sub> at 1 mg/L > UV/H<sub>2</sub>O<sub>2</sub> at 1 mg/L > VUV/H<sub>2</sub>O<sub>2</sub> at 5 mg/L ≈ UV/H<sub>2</sub>O<sub>2</sub> at 5 mg/L. The calculated EE/O values for all the treatment processes, including VUV treatment, were <10, indicating the economic feasibility of the processes.

### 3.4. Formation of by-products from NOM and inorganic ions

#### 3.4.1. THMFP

THMs in chlorinated drinking water are associated with increased cancer risk (Cantor et al., 1998). The WHO has established guideline values for four THM species: bromoform, DBCM, BDCM, and chloroform (100, 100, 60, and 200 µg/L, respectively). In the United States, individual THMs are not regulated, but total THMs (i.e., the sum of the concentrations

of the above-mentioned 4 THMs) is regulated (annual average, 80 µg/L). In Japan, regulation values for bromoform, DBCM, BDCM, chloroform, and total THMs have been established at 90, 100, 30, 60, and 100 µg/L, respectively.

The THMFP of the raw lake water used in our experiments was 100 µg/L (Fig. 6(a)); chloroform and BDCM accounted for approximately 70% and 25%, respectively, of the total THMs produced. A small amount of DBCM was observed (approximately 5%), and no bromoform was detected. The chloroform concentration exceeded the Japanese Drinking Water Quality Standard (JDWQS). VUV treatment decreased THMFP by 22%. The hydrophobic fraction of NOM has been reported to show the greatest ability to produce CDBPs (Chang et al., 2001). Because VUV irradiation effectively decomposes the hydrophobic fraction of NOM (Buchanan et al., 2005), it is likely that the possible precursors of THMs were decomposed by VUV treatment, resulting in the observed decrease in THMFP. Buchanan et al. (2006) reported that THMFP increased with 32 J/cm<sup>2</sup> of VUV irradiation that was much higher than the VUV dose applied in the present study. These investigators presumed that the increase was due to the halogenation of low molecular weight compounds produced by the breakdown of large NOM compounds with the VUV irradiation. In contrast, in the present study, THMFP decreased with the VUV irradiation, of which dose was much lower than the dose applied in these investigators. The breakdown of large NOM compounds may not occur with the low VUV dose applied in the present study. The chloroform formation potential was decreased by VUV treatment, whereas the DBCM and BDCM formation potentials did not change. The precursors of chloroform in the raw lake water were likely decomposed to compounds that did not produce chloroform after chlorination, whereas the precursors of DBCM and BDCM may have been converted to compounds that did produce DBCM and BDCM after chlorination.

The chloroform formation potential was decreased further by both BAC and virgin GAC treatment; the removal percentages were 66% and 93%, respectively. The BDCM formation potential was not decreased by BAC treatment but was decreased by virgin GAC treatment. The DBCM formation potential was not decreased by either the BAC treatment or the virgin GAC treatment. Overall, BAC treatment decreased THMFP by 46%, and virgin GAC treatment reduced it by 81%, owing to the large reduction in the precursors of the predominant species (chloroform) by these treatment processes. Buchanan et al. (2008) reported that VUV/BAC treatment decreased THMFP, in agreement with our results. However, these investigators reported that the formation potentials of all THM species were decreased by the VUV/BAC treatment.

The THMFP of the groundwater was very low (2 µg/L, Fig. 6(b)), which we attributed to the low DOC concentration in the groundwater, and remained low (<8 µg/L) after the VUV, VUV/BAC, and VUV/GAC treatments.

#### 3.4.2. HAAFP

HAAs are a public health concern owing to their potential genotoxicity and carcinogenicity (Richardson et al., 2007). We measured the formation potentials of 9 HAAs, including five species (BAA, CAA, DBAA, DCAA and TCAA) regulated under the designation HAA<sub>5</sub> by the United States Environmental Protection Agency (USEPA; 60 µg/L as an annual average), two species with established WHO guideline values (DCAA and TCAA; 50 and 200 µg/L, respectively), and three species listed