

## Occurrence of preservatives and antimicrobials in Japanese rivers

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## Abstract

We established a method for the simultaneous analysis of seven preservatives and five antimicrobials in water. These chemicals are widely used in cosmetics, and their presence in river water is of concern. We used the method to test 13 sites in Japanese rivers and streams contaminated by domestic wastewater, effluent, or industrial wastewater. 2-Phenoxyethanol (2-PE), isopropylmethylphenol, resorcinol, and triclosan were detected at most sites; the maximum concentration of 2-PE detected was 14 000 ng L<sup>-1</sup>. The results suggest that the major sources of 2-PE were cosmetics and household detergents. The ratio of methylparaben to *n*-propylparaben in river waters with direct wastewater drainage was similar to that in common cosmetics. This is the first research on levels of 2-PE, isopropylmethylphenol, and chlorphenesin in river water.

Keywords: preservatives; antimicrobials; cosmetics; 2-Phenoxyethanol; Isopropylmethylphenol; river water.

## 1. Introduction

Preservatives and antimicrobials are used in a wide range of soaps, toothpastes, cosmetics, hair styling products, sunscreens, and other daily personal care products (PCPs). Most are used to suppress microorganism growth in products. PCPs thus enter waters from households. Some of the components are not efficiently removed by wastewater treatment (McAvoy et al., 2002; Nakada et al., 2007; Kasprzyk-Hordern et al., 2009), and in unsewered areas, they enter waterways without appropriate treatment. Components of PCPs are among the most commonly detected compounds in surface waters throughout the world (Kolpin et al., 2002; Moldovan, 2006; Kasprzyk-Hordern et al., 2008). Triclosan (TCS) can induce the expression of resistance and cross-resistance mechanisms in bacteria (Orvos et al., 2002; Tatarazako et al., 2004; Dussault et al., 2008). Its occurrence in surface waters and wastewaters has been extensively studied (Kolpin et al., 2002; McAvoy et al., 2002; Loraine et al., 2006; Cuderman et al., 2007; Trenholm et al., 2008; Kasprzyk-Hordern et al., 2009; Pedrouzo et al., 2009). Some reported concentrations in widely separated regions are high enough to trigger bacterial resistance in the environment also (SCCS, 2010). Furthermore, TCS has been detected in drinking water (Loraine et al., 2006).

However, other preservatives or antimicrobials have not been thoroughly studied. Those

used in large quantities in cosmetics are regulated in Japan (Ministry of Health and Welfare Notification of Japan, 2000). The standard for preservatives and antimicrobials in cosmetics lists about 50 ingredients, including 2-phenoxyethanol (ethylene glycol monophenyl ether: 2-PE) and parabens in lotions, resorcinol (1,3-benzenediol: RC) in hair dyes, TCS in hand soap, and isopropylmethylphenol (4-isopropyl-3-methylphenol: IPMP) in toothpaste and hand soap. 2-PE and RC are also included in the Organisation for Economic Co-operation and Development's (OECD) list of high-production-volume chemicals.

In recent years, 2-PE, a preservative, has been extensively used as a substitute for or in combination with parabens in cosmetics in Japan. Parabens are still used widely in cosmetics and foods. IPMP has come to be used in hand soaps and toothpastes as a substitute for TCS, which was shown to be toxic to aquatic organisms (SCCS, 2010). 2-PE, parabens, and benzoic acid are used most frequently, followed by chlorphenesin (CP), dehydroacetic acid, sorbic acid, and chloroxylenol (4-chloro-3,5-xyleneol: PCMX) as antibacterial agents in cosmetics (Mori et al., 2007). CP and dehydroacetic acid are used in skin lotions and creams for the treatment of acne; sorbic acid in foundations; and PCMX in deodorants, baby powders and creams. However, little information is available on their occurrence and ecotoxicity in water, as their analyses depend on specific methods. The objective of this study was to establish an analytical method to simultaneously measure a number of preservatives and antimicrobials in surface waters, and to obtain analytical data on their occurrence in the environment.

We present a method for the simultaneous determination of commonly used preservatives and antimicrobials in surface waters, and tested 13 sites in Japanese rivers contaminated by domestic wastewater, sewage treatment plant (STP) effluent, or industrial wastewater.

## 2. Materials and methods

### 2.1. Reagents and standards

The method covers seven preservatives and five antimicrobials (**Table 1**). 2-PE (>98.5% purity), methylparaben (MeP) (>99.0%), IPMP (>99.0%), RC (>99.0%), and PCMX (>98.0%) came from Wako Pure Chemical Industries, Japan. Ethylparaben (EtP) (>98.5%), *n*-propylparaben (*n*-PrP) (>98.5%), isopropylparaben (*i*-PrP) (>98.5%), *n*-butylparaben (*n*-BuP) (>98.5%), and isobutylparaben (*i*-BuP) (>98.5%) came from Kanto Chemical Co., Japan. CP (>98.5%) came from Alfa Aesar GmbH & Co. KG, Germany. TCS (>96.0%) came from Tokyo Chemical Industry, Japan. RC-2,4,5,6-d<sub>4</sub>, TCS-d<sub>3</sub> (Toronto Research Chemicals Inc.),

2-PE-d<sub>4</sub>, MeP-d<sub>4</sub>, and *n*-PrP-d<sub>4</sub> (C/D/N Isotopes) were used as surrogates. The derivatizing reagent N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) came from Thermo Fisher Scientific Inc., USA.

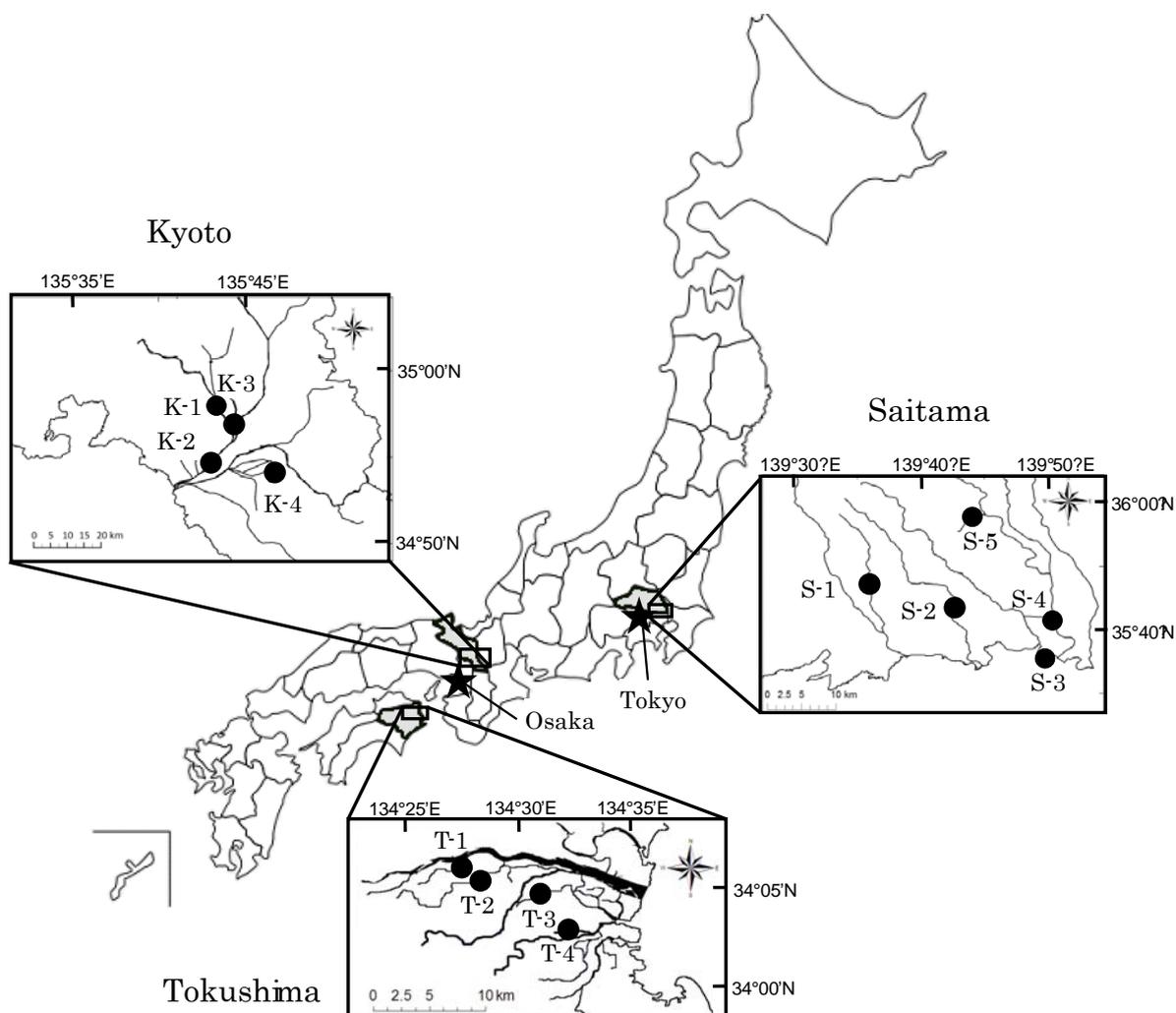
## 2.2. Sample collection

River water samples were collected from four sites in Tokushima (T-1–4), four in Kyoto (K-1–4), and five in Saitama (S-1–5) (**Fig. 1**) during autumn 2010 and winter 2011. The Tokushima sites were small urban streams in an unsewered area; only T-1 was downstream of a community scale STP which served a small residential area. K-1 was a point on a river which flows through an area where 80% of the population is served with sewerage. Approximately 40% of total surface water at K-2 is sewage effluent. Almost all of the river water at K-3 consisted of treated wastewater. The water at K-4 contains wastewater from a hospital and residential aerobic septic tanks. All sites in Saitama were contaminated with industrial and domestic wastewater. Up to 80% of the population is served with sewerage. S-5 was located on a stream that flows through an area of low service coverage with many farms upstream. S-4 was sampled only in autumn and S-5 in winter.

## 2.3. Sample extraction

The samples were kept in cooled boxes and transported to the laboratory, where they were filtered through glass fiber filters (GF/C, Whatman) as soon as possible. The time elapsed between sampling in the field and filtering in the laboratory ranged from several hours and to 48 hours. The particulate phase was not analyzed. The samples (1000 mL) were spiked with 200 ng of surrogates (RC-d<sub>4</sub>, TCS-d<sub>3</sub>, 2-PE-d<sub>4</sub>, MeP-d<sub>4</sub>, and *n*-PrP-d<sub>4</sub>). They were then extracted by solid-phase extraction through tandem cartridges: Oasis HLB Plus type 225 mg (Waters Corp.) and InertSep SlimJ Pharma FF 230 mg (GL Sciences Inc.). The recovery of RC by the Oasis HLB was poor, but that by the InertSep SlimJ Pharma was sufficient. Both cartridges were conditioned first with ethyl acetate, methanol, and ultrapure water. The samples were passed through the cartridges at 10 mL min<sup>-1</sup>. After sample loading, the cartridges were separated and the water in them was removed by syringe and centrifugation. Each cartridge was backflush-eluted with 8 mL ethyl acetate at 1 mL min<sup>-1</sup> using a Sep-Pak Elution pump (Waters Corp.). Both extracts were mixed and the water phase was removed with a Pasteur pipette. The solvent phase was reduced under a gentle stream of nitrogen at 40 °C until close to dryness, and the residue was then redissolved in 100 µL dichloromethane.

The extracts were not cleaned up further, because some of the matrix was left in the green to brown aqueous phase.



**Fig. 1.** Sampling sites in Tokushima, Kyoto and Saitama, Japan.

As procedural blanks revealed small amounts of 2-PE and MeP, the concentrations were corrected by the blanks. Special care was taken to minimize sample contamination. All glassware was rinsed several times with acetone and ethyl acetate just before usage.

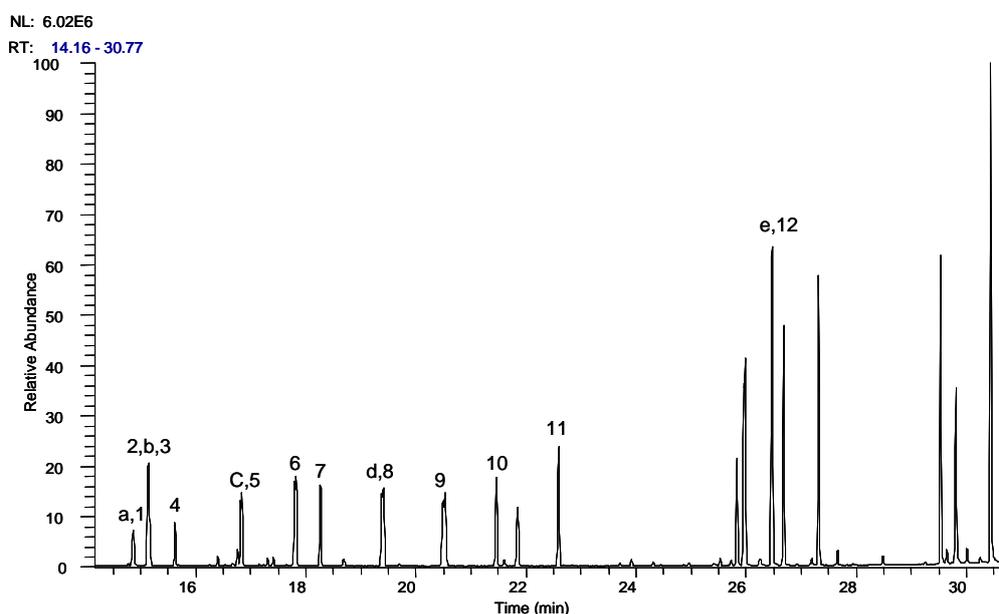
#### 2.4. BSTFA derivatization

Derivatization of hydroxylated chemicals is advantageous for gas chromatography – mass spectrometry (GC-MS) analysis. The extracts dissolved in 100  $\mu$ L dichloromethane were derivatized with 100  $\mu$ L BSTFA at 40 °C for 1 h to increase the sensitivity and limits of

detection of the hydroxylated target compounds.

## 2.5. Instrumental analysis

Chemical analysis was performed by GC (Trace GC) interfaced with an ion trap MS (Polaris-Q; Thermo Fisher Scientific Inc.) equipped with a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., Agilent Inc.). The carrier gas was helium at a constant flow of 1.0 mL min<sup>-1</sup>. The injector was operated in splitless mode (250 °C), and the injection volume was 2 μL. The oven temperature program started at 50 °C (held for 1 min), ramped at 20 °C min<sup>-1</sup> to 80 °C (held for 3 min), then increased at 20 °C min<sup>-1</sup> to 100 °C (held for 3 min), then at 10 °C min<sup>-1</sup> to 180 °C (held for 3 min), then 10 °C min<sup>-1</sup> to 300 °C (held for 10 min). The transfer line temperature was at 280 °C. The MS was operated in electron ionization mode with an energy of 70 eV. The ion source temperature was 250 °C. The mass range was 50 to 540 *m/z* in full-scan mode. A representative total ion chromatogram of a standard mixture is shown in **Fig. 2**. The quantifying ion, confirmatory ion, and surrogate for each analyte are shown in the supporting information (**Table S1**).



**Fig. 2.** GC-MS total ion chromatogram of standard mixture (1 000 μg L<sup>-1</sup>).

(a) 2-PE-d<sub>4</sub>; (b) RC-d<sub>4</sub>; (c) MeP-d<sub>4</sub>; (d) n-PrP-d<sub>4</sub>; (e) TCS-d<sub>3</sub>.

(1) 2-PE; (2) IPMP; (3) RC; (4) PCMX; (5) MeP; (6) EtP; (7) i-PrP; (8) n-PrP; (9) i-BuP; (10) n-BuP; (11) CP; (12) TCS.

### 3. Results and discussion

#### 3.1. Procedural recoveries

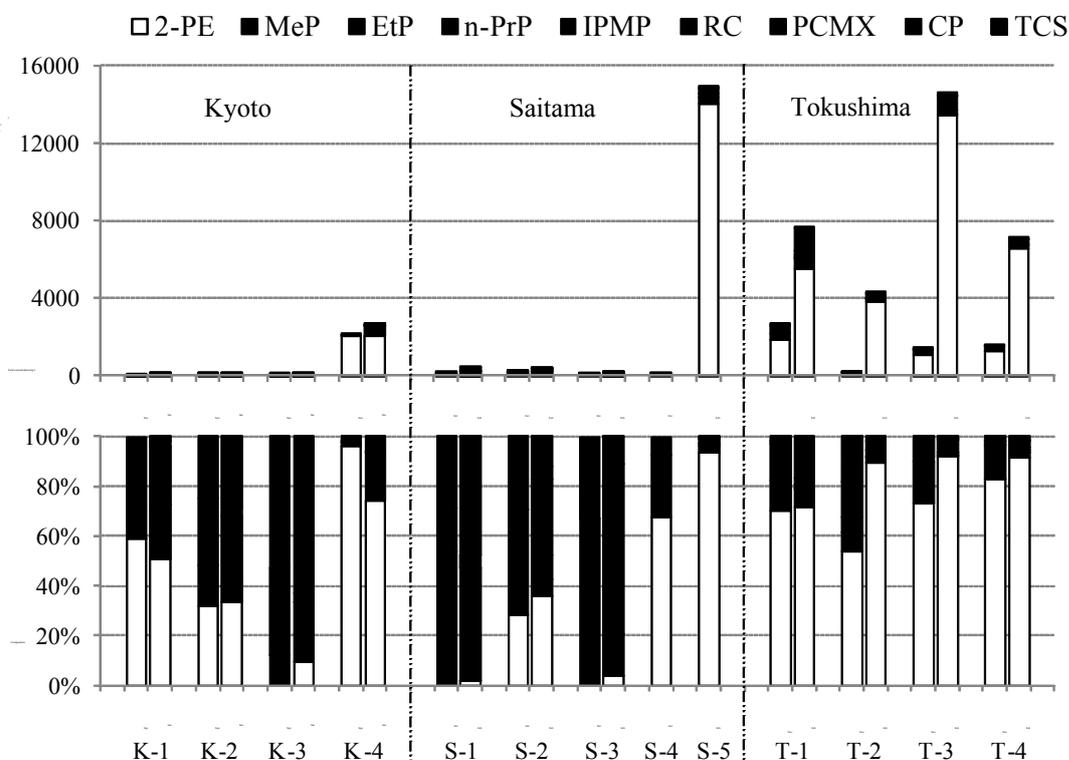
Reproducibility was examined with five replicate analyses of 1000 mL of ultrapure water spiked with 4 ng of standard chemicals. The quantity was set so that the final concentration before analysis should be the lowest on the calibration curves ( $20 \mu\text{g L}^{-1}$ ). The reproducibility of the surface water samples was determined also with five replicate analyses. Filtered surface water samples were spiked with 20  $\mu\text{L}$  of standard solution ( $10 \text{ mg L}^{-1}$ ). The limits of quantification (LOQs) ranged from 0.6 to  $2.4 \text{ ng L}^{-1}$ , and the recovery rates ranged from 89.7% to 122% (**Table 2**). Recovery was deemed sufficient.

#### 3.2. Occurrence of preservatives in surface waters

2-PE, IPMP, RC, and TCS were detected at all sites (**Fig. 3, Table S1**). In contrast, *i*-PrP, *n*-BuP, and *i*-BuP were not detected in any samples. Concentrations of the sum of the 12 target compounds ranged from 37.9 to  $14\,900 \text{ ng L}^{-1}$ , with a median of  $288 \text{ ng L}^{-1}$  among the 24 sampling data. The total concentration was highest at S-5, where 2-PE accounted for more than 90% of the total ( $14\,000 \text{ ng L}^{-1}$ ). In addition, at all sites in Tokushima, 2-PE had the highest concentration among the target compounds; for example, 2-PE concentrations at T-3 and T-4 were  $13\,400 \text{ ng L}^{-1}$  and  $6\,540 \text{ ng L}^{-1}$ , respectively (Both are more than 90% of the total). These sites are located along small streams that receive direct domestic wastewater discharge. These concentrations are comparable to those in the influent of an STP in the USA:  $8\,800\text{--}22\,000 \text{ ng L}^{-1}$  (Trenholm et al., 2008). 2-PE is used in various cosmetics as a substitute for parabens, and is extensively used in skin lotions, body cream, lipstick, and shampoo in Japan (Nakajima, 2011). The total amount of its domestic manufacture and import was at least 6 000 t in 2011 (METI, 2013.). On the other hand, it is highly degradable in the environment (Tamura et al., 2012). Therefore the cause of its occurrence in high concentrations might be high emission from domestic use. In contrast, the concentrations of 2-PE at the sampling sites with little direct domestic wastewater input (K-1–3, S-1–4) were much lower N.D.– $139 \text{ ng L}^{-1}$  similar to those in final effluent of an STP (Trenholm et al., 2008; Jonkers et al., 2010).

MeP, EtP, and *n*-PrP were detected in some samples. The concentrations of MeP ranged from N.D. to  $525 \text{ ng L}^{-1}$ . MeP also was detected at high concentrations in Tokushima and at S-5, comparable to those downstream of a sewage outfall in a residential community in China (Peng et al., 2008). The concentrations of *n*-PrP ranged from N.D. to  $181 \text{ ng L}^{-1}$ . MeP, *n*-PrP,

and 2-PE were often detected simultaneously. EtP was detected only in Tokushima, with concentrations ranging from N.D. to 73.6 ng L<sup>-1</sup>. This result was comparable to previous results in the same rivers (Yamamoto et al., 2011), and lower than MeP and *n*-PrP.



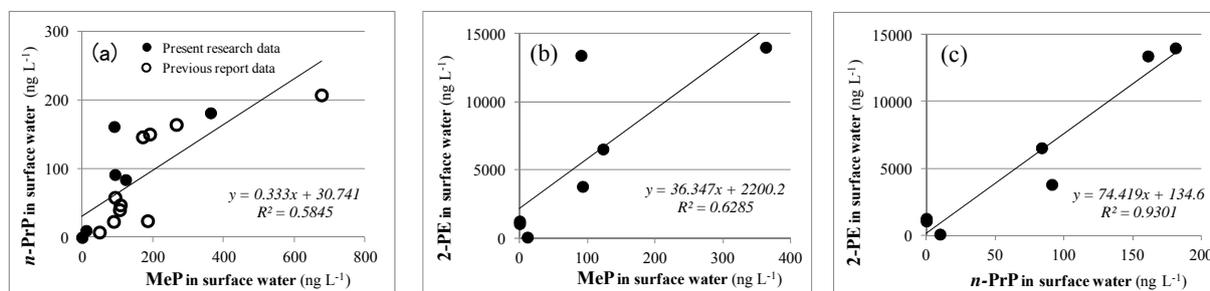
**Fig. 3.** Concentrations (upper graph) and compositions (lower graph) of preservatives and antimicrobials in surface waters in Kyoto, Saitama, and Tokushima. Chemicals not detected were excluded.

### 3.3. Sources of preservatives in surface water with direct domestic wastewater discharge

Data from sampling sites with significant impact of household wastewater were used to compare compositions of 2-PE, MeP, and *n*-PrP in surface waters and cosmetic products (S-5, T-2–4) (Figs. 4, S1). There was a significant linear relation between MeP and *n*-PrP in cosmetic products ( $P < 0.0001$ ; Fig. S1(a)). MeP and *n*-PrP are often used together in cosmetics for their synergistic preservative effects (Okamoto, 2008). The ratio of MeP to *n*-PrP in river waters was 0.33, close to that in cosmetics products (0.26), though MeP degrades a little faster than *n*-PrP (González-Mariño et al., 2011). These results indicate that MeP and *n*-PrP in these river water samples originated from quotidian cosmetic products. Parabens have been detected at high concentrations in human urine samples, but most are conjugated (Wang et al., 2013). We measured only free parabens, so observed relations between

environment and products may be due to the direct discharge of parabens in products, not to the excretion through human body.

On the other hand, 2-PE had significant correlations with MeP and *n*-PrP in surface waters, in spite of there being no significant relationships in cosmetic products and rapid degradation in the aquatic environment (OECD, Existing Chemical Database; Tamura et al., 2012). It is difficult to explain these correlations only from the concentration ratios in cosmetic products. These results suggest other possible major sources of 2-PE in surface waters, such as household cleaners and detergents, which can contain a large amount of 2-PE (Scognamiglio et al., 2012). These relationships could be associated with the consumption of cleaners and detergents and with the population size in each catchment.



**Fig. 4.** Correlations among MeP, *n*-PrP, and 2-PE in surface waters. Previous data are taken from Yamamoto et. al. (2011).

(a) MeP vs. *n*-PrP, (b) MeP vs. 2-PE, (c) *n*-PrP vs. 2-PE.

### 3.4. Antimicrobials in surface waters

IPMP and TCS were detected at all sites, even those with no direct wastewater drainage. This is the first research to report concentrations of IPMP in the aquatic environment. The concentration of IPMP ranged from N.D. to 715 ng L<sup>-1</sup>. The highest concentration was found at T-3, which received direct wastewater discharge. In recent years, IPMP has been extensively used as an alternative to TCS in toothpastes, deodorants, and acne lotions and creams in Japan. This may explain its higher concentrations than of TCS in many samples (**Fig. 3**). IPMP is persistent in the environment (Tamura et al., 2012). Thus, IPMP is expected to remain in the aquatic environment for several days. Although IPMP has less adverse effects on aquatic organisms than TCS (Tamura et al., 2012), its increasing usage in PCPs will necessitate an ecological risk assessment.

TCS was detected in the range of N.D.–177 ng L<sup>-1</sup>. Relatively high concentrations were found in Tokushima at sites where large amounts of untreated domestic wastewater flow into

the streams. However, even at K-3, where the river water consists almost completely of treated wastewater, the TCS concentration was also slightly elevated (70.7 and 86.7 ng L<sup>-1</sup>). K-3 was affected by effluent from two wastewater treatment plants (WWTPs) located upstream, both of which use activated sludge treatment. The concentrations of TCS at K-3 were similar to those in the effluent from other Japanese WWTPs that use activated sludge (Nakada et al. 2006). We found little difference in the concentrations of TCS between the sites with and without a sewerage service. A possible explanation for the lack of difference is the very small population of Tokushima, and the consequent minimal usage of TCS. On the other hand, the STP effluent at K-3 could not be diluted. Further investigation is necessary for analysis of the influent at the WWTPs upstream.

The concentrations of RC ranged from 1.2 to 1 150 ng L<sup>-1</sup>. RC was detected in all samples, although there were no significant correlations with 2-PE, MeP, or IPMP. Therefore, the source of RC in surface waters may not be cosmetic products or household cleaners. About half of RC is used by the rubber industry. RC is also used in preparations for the topical treatment of skin conditions such as acne, and in oxidative hair dyes (WHO, 2006). As a monomeric byproduct of the reduction, oxidation, and microbial degradation of humic substances (WHO, 2006), RC is also found in natural products. Our data should have included these “background” quantities as well.

The use of CP in sunscreens and makeup removers has increased remarkably in Japan (Mori et al., 2007). Yet CP was detected only at S-1 (164 ng L<sup>-1</sup>) and S-2 (18.4 ng L<sup>-1</sup>) in winter. As far as we know, this is the first report of the levels of CP in the environment. PCMX is used in deodorants, baby powders, creams, and other cosmetics. It was detected only in the autumn sample at T-1, at a concentration (17.8 ng L<sup>-1</sup>) lower than in river waters in England (Kasprzyk-Hordern et al., 2009). Since there is yet little information about CP and PCMX in the aquatic environment, further research on their occurrence in water and their behavior in WWTPs may be necessary.

#### 4. Conclusions

Our method allows the simultaneous analysis of seven preservatives and five antimicrobials in surface waters. Trimethylsilyl derivatization allowed very good chromatographic separation and sensitive and accurate determination of the target compounds.

The method detected four preservatives and five antimicrobials in river waters in Japan. 2-PE, IPMP, RC, and TCS were consistently detected, some at high concentrations (maxima

of 14 000, 715, 1 150, and 177 ng L<sup>-1</sup>, respectively). This is the first report of the occurrence of 2-PE, IPMP, and CP in river water. 2-PE and IPMP were detected at most sites. In particular, 2-PE was detected at >10 000 ng L<sup>-1</sup> in areas with no or little sewerage. The concentration profile suggests that the source of the 2-PE was both cosmetic products and household detergents. The ratio of MeP to *n*-PrP in waters with direct wastewater discharge was similar to that in cosmetic products used in daily life. 2-PE, MeP, and *n*-PrP are likely to be “pseudopersistent” pollutants on account of their short half-lives. Further investigations are necessary to evaluate the ecological risks of 2-PE and IPMP, which were detected frequently at high concentrations.

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**Table 1.** Characteristics of preservatives and antimicrobials investigated in this study.

Abbreviation of substance in this study	Chemical names	CAS	Structure	MW (g/mol)	LogKow
<i>preservatives</i>					
<b>2-PE</b>	2-Phenoxyethanol	122-99-6		138.16	1.2 <sup>a</sup>
<b>MeP</b>	Methyl <i>p</i> -hydroxybenzoate	99-76-3		152.15	1.96 <sup>b</sup>
<b>EtP</b>	Ethyl <i>p</i> -hydroxybenzoate	120-47-8		166.17	2.47 <sup>b</sup>
<b><i>n</i>-PrP</b>	<i>n</i> -Propyl <i>p</i> -hydroxybenzoate	94-13-3		180.20	3.04 <sup>b</sup>
<b><i>i</i>-PrP</b>	Isopropyl <i>p</i> -hydroxybenzoate	4191-73-5		180.20	2.91 <sup>c</sup>
<b><i>n</i>-BuP</b>	<i>n</i> -Butyl <i>p</i> -hydroxybenzoate	94-26-8		194.23	3.57 <sup>b</sup>
<b><i>i</i>-BuP</b>	Isobutyl <i>p</i> -hydroxybenzoate	4247-02-3		194.23	3.40 <sup>c</sup>
<i>antimicrobials</i>					
<b>IPMP</b>	4-Isopropyl-3-methylphenol	3228-02-2		150.22	3.52 <sup>c</sup>
<b>RC</b>	Resorcinol	108-46-3		110.11	0.79-0.93 <sup>d</sup>
<b>PCMX</b>	4-Chloro-3,5-xyleneol	88-04-0		156.6	3.25 <sup>e</sup>
<b>CP</b>	3-(4-Chlorophenoxy)-1,2-propanediol	104-29-0		202.63	1.50 <sup>c</sup>
<b>TCS</b>	2,4,4'-Trichloro-2'-hydroxydiphenyl Ether	3380-34-5		289.55	4.76 <sup>e</sup>
<i>UV filters</i>					
<b>BP-1</b>	2,4-Dihydroxybenzophenone	131-56-6		214.22	2.96 <sup>f</sup>
<b>BP-2</b>	2,2',4,4'-Tetrahydroxybenzophenone	131-55-5		246.21	2.92 <sup>f</sup>
<b>BP-3</b>	2-Hydroxy-4-methoxybenzophenone	131-57-7		228.24	3.79 <sup>e</sup>
<b>BP-6</b>	2,2'-Dihydroxy-4,4'-dimethoxybenzophenone	131-54-4		274.27	3.90 <sup>c</sup>

a International Chemical Safety Cards ICSC0538

b Hansch, C., A. Leo and D. Hoekman (1995): Exploring QSAR-Hydrophobic, Electronic and Steric Constants, American Chemical Society

c US EPA, 2011. Estimation programs interface suite™ for Microsoft® Windows, v 4.10. Environmental Protection Agency, Washington, DC, USA (<http://www.epa.gov/opptintr/exposure/pubs/episuite.html>)

d International Chemical Safety Cards ICSC1033

e Philip H. Howard, William M. Meylan, Handbook of Physical Properties of Organic Chemicals

f Zifeng, et al., 2011

**Table 2.** Estimated limits of quantification and recoveries used for correction (n = 5 replicates)

Compound	LOQ (ng L <sup>-1</sup> )	Recovery (%) ±SD
2-PE	0.9	115 ± 16
MeP	0.8	106 ± 8.1
EtP	1.0	107 ± 9.8
<i>i</i> -PrP	0.6	95.2 ± 2.7
<i>n</i> -PrP	0.6	95.2 ± 3.3
<i>i</i> -BuP	2.4	89.7 ± 5.1
<i>n</i> -BuP	1.0	93.9 ± 5.1
RC	0.9	103 ± 3.1
IPMP	1.1	120 ± 17
PCMX	0.9	121 ± 8.1
CP	1.4	90.4 ± 11
TCS	2.0	122 ± 20