

Source-specific sewage pollution detection in urban river waters using pharmaceuticals and personal care products as molecular indicators

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Abstract Source-specific elucidation of domestic sewage pollution caused by various effluent sources in an urban river water, as conducted for this study, demands knowledge of the relation between concentrations of pharmaceuticals and personal care products (PPCPs) as molecular indicators (caffeine, carbamazepine, triclosan) and water quality concentrations of total nitrogen (T-N) and total phosphorous (T-P). River water and wastewater samples from the Asahikawa River Basin in northern Japan were analyzed using derivatization-gas chromatography/mass spectrometry. Caffeine, used as an indicator of domestic sewage in the Asahikawa River Basin, was more ubiquitous than either carbamazepine or triclosan (92–100 %). Its concentration was higher than any target compound used to assess the basin: <4.4–370 ng/L for caffeine, <0.6–3.9 ng/L for carbamazepine, and <1.1–13 ng/L for triclosan. Higher caffeine concentrations detected in wastewater effluents and the strongly positive mutual linear correlation between caffeine and T-N or T-P ($R^2 > 0.759$) reflect the contribution of septic tank system effluents to the lower Asahikawa River Basin. Results of relative molecular indicators in combination with different molecular indicators (caffeine/carbamazepine and triclosan/carbamazepine) and cluster analysis better reflect the contribution of sewage than results

obtained using concentrations of respective molecular indicators and cluster analysis. Relative molecular indicators used with water quality parameters (e.g., caffeine/T-N ratio) in this study provide results more clearly, relatively, and quantitatively than results obtained using molecular indicators alone. Moreover, the caffeine/T-N ratio reflects variations of caffeine flux from effluent sources. These results suggest strongly relative molecular indicators are also useful indicators, reflecting differences in spatial contributions of domestic sources for PPCPs in urban areas.

Keywords Emerging contaminants · Molecular indicator · Sewage pollution · Total nitrogen · Aerobic septic tank systems · Urban river water · PPCPs

Introduction

Domestic sewage pollution is an important concern related to water quality for human health and ecosystems because it exacerbates eutrophication and bacterial and organic chemical contamination in aquatic environments. Particularly, pharmaceuticals and personal care products (PPCPs) and their adverse effects on aquatic environments are a growing global concern (UNEP, 2013). Many PPCPs do not exhibit acute aquatic toxicity. Nevertheless, nontarget aquatic organisms, terrestrial ecosystems, and human health are degraded severely by long-term exposure to low concentrations of PPCP mixtures (Moldovan 2006; Rabiet et al. 2006). These PPCPs are detected frequently in any water body affected by treated or untreated sewage as a result of consistent input from various domestic and veterinary sources (Veach and Bernot 2011; Wu et al. 2014).

Contamination sources for human-use PPCPs in water bodies are mainly effluents from centralized sewer systems such as wastewater treatment plants (WWTPs) in urban areas and

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decentralized sewer systems such as septic tank systems (STSs) and local sewage treatment plants (LSTPs) in rural and suburban areas. These decentralized sewer systems, especially considering rapid and expansive land development, have been more cost-effective and more available than centralized sewer systems that involve WWTPs (U.S. Environmental Protection Agency 2000). Especially, conventional STSs in the USA and Europe discharge effluent into soil with no advanced treatment for human-use PPCPs (Carrara et al. 2008). Consequently, pharmaceuticals of several types and other trace contaminants reach groundwater systems via on-site system wastewater infiltration (Cody 2010). Reportedly, conventional STSs in rural and suburban areas in the USA and Europe can cause groundwater and seawater contamination by PPCPs (U.S. Environmental Protection Agency 2000). Therefore, septic tanks equipped with aerobic treatment units, known as aerobic STSs (ASTSs), are used to replace conventional STSs, which have become a major source of groundwater and surface water pollution in some areas. Reportedly, the quality of effluent from ASTSs is superior to that from conventional STSs (U.S. Environmental Protection Agency 2000).

Wastewater treatment by ASTSs for the combined treatment of toilet water and gray water from various domestic sources such as kitchens, bathrooms, and laundry machines has probably equal or lower efficiency compared to that of WWTPs (Nakada et al. 2007). In addition, gray water generally includes higher nitrogen and phosphorous concentrations than those of wastewater from ASTSs. Therefore, when discharged directly into a receiving water body, they can cause surface water pollution. Reportedly, crowded areas of STSs present an unusually high risk for the transport of human-derived contaminants to nearby coastal systems via groundwater (Gardinali and Zhao 2002; Singh et al. 2010). In Japan, ASTSs have become increasingly used as decentralized systems for domestic sewage. They often exist in urban areas where centralized sewer services are currently unavailable. The performance of their aging systems generally deteriorates over time because of a lack of maintenance and system failure. Particularly, it is difficult to identify the contribution of such failing ASTSs clearly and individually in densely populated and urban areas. Therefore, the development of domestic source tracking techniques is important to clarify and reduce the effects of domestic sewage pollution from such failing ASTSs. Moreover, the effects of human-use PPCPs from ASTSs depend strongly on sewerage coverage populations in river basins (Nakada et al. 2007). Nevertheless, few studies of PPCPs have been conducted in such areas for small urban rivers in metropolitan areas in Japan (Komori and Suzuki 2009) or for major rivers in Japan (Nakada et al. 2006; Nakada et al. 2007).

Organic compounds, such as PPCPs, that are specific to certain pollutant sources of sewage are useful as molecular indicators for identifying pollutant sources and their transport pathways (Nakada et al. 2008; Buerge et al. 2003). Therefore,

a suitable selection of molecular indicators is anticipated as a useful tool for the quantitative examination of PPCPs from various effluent sources. Reportedly, carbamazepine, diethyltoluamide, and caffeine are potential sewage indicators in river water (Glassmeyer et al. 2005). Carbamazepine was proposed as a persistent sewage indicator because it is one of the most frequently detected pharmaceuticals in WWTPs, river water, and seawater (Miao and Metcalfe 2003). Caffeine is a useful marker for untreated wastewater from combined sewer outflows (CSOs) (Buerge et al. 2003). Crotamiton, carbamazepine, and mefenamic acid have also been useful molecular indicators in coastal environments (Nakada et al. 2008). The utility of these molecular indicators for domestic sewage mainly emphasizes the characteristics of concentration variation in water bodies. However, changes in river water flow and discharge from domestic sources necessarily affect their concentrations. They might be regarded as a site-specific indicator in the study areas. Therefore, some relative indicator for the contribution of domestic sewage must be identified to facilitate relative comparisons among such areas. Furthermore, such a study is expected to prove useful in tracking the source of PPCPs in water bodies. A few studies of relative indicators using PPCPs intended for veterinary use in livestock wastewaters have been conducted in Japan and other Asian countries (Murata et al. 2011; Shimizu et al. 2013). No information for relative indicator using human-use PPCPs with water quality parameters as total nitrogen (T-N) and phosphorous (T-P) in river water and wastewaters is available in the relevant literature, but single- and multiple-regression analyses have been conducted to clarify the relation between PPCPs and water quality parameters (Veach and Bernot 2011; Bernot et al. 2013; Yang et al. 2013; Wu et al. 2014).

To elucidate source-specific domestic sewage pollution caused by various effluent sources to urban river water, we assessed the relation between concentrations of human-use pharmaceuticals (caffeine and carbamazepine) and a personal care product (triclosan) and water quality parameters as total nitrogen (T-N) and total phosphorous (T-P) within the Asahikawa River Basin (Asahikawa and Taiheigawa River) in northern Japan. Detection frequencies, concentrations, spatial concentration variations, and fluxes of target compounds are also examined in this case study. Furthermore, caffeine/carbamazepine, triclosan/carbamazepine, caffeine/T-N, and caffeine/T-P ratios were compared as relative molecular indicators of contribution of domestic sewage with those of other urban river waters.

Materials and methods

Study area

The Asahikawa River Basin, located in central Akita, northern Japan, includes the Asahikawa River and the Taiheigawa

River, which is the largest tributary of the Asahikawa River. Figure 1 portrays a map of the river basin, including the sampling locations. The drainage area of the Asahikawa River Basin is 227 km², of which the Asahikawa River’s drainage area is 75 km². It flows 21.8 km from a source to the Kyu-Omonogawa River (Akita Canal); then it flows into the Sea of Japan. The Taiheigawa River’s drainage area is 152 km². It flows 26.3 km from the sources to the lower Asahikawa River near downstream of site T8. The river water is used mainly for rice paddy irrigation.

According to the Akita City Comprehensive Urban Master Plan (Akita City 2011.3), about 300,000 people live in Akita City (ca. 906 km²). The share of the sewered population in Akita City is ca. 87 %. East, south, and central districts in Akita City (ca. 239 km²) are included within the basin, where ca. 190,000 people reside. The basin comprises approximately 40 % forest, 10 % agricultural, and 50 % residential, commercial, and industrial areas.

Sites A1 and A2 in the upper river basin are mainly forest areas. A WWTP, which has a small separated sewer system (WWTP1), was developed around site A1. Site A3 is regarded as an agricultural and forest area. Small villages exist along the river. Only an ASTS covers those areas. Sites A4 and A5 are mainly residential areas. Both separate sewer system (WWTP3) and ASTS covers those areas. Sites A6–A11 are mainly residential, commercial, and industrial areas in the central district. The combined sewer system (WWTP2) covers almost all of those areas. In addition, CSO points are located

near sites A6–A10. Site A11 is located at the boundary areas of combined and separated sewer system. Site A12 is located in the Akita Canal, 1.5 km downstream of the Asahikawa River mouth.

Sites T1 and T2 are agricultural and forest areas with small villages along the river. An ASTS covers those areas. Site T3 mainly includes agricultural areas. Sites T4–T6 are regarded as agricultural, residential, and commercial areas. Both separated (WWTP3) and decentralized (LSTPs and ASTSs) sewer systems cover those areas. In addition, several outflow points from urban storm drainage systems are located between site T4 and upstream of site T7 within the separated sewer system area (WWTP3). Agricultural water outflow is also discharged upstream of site T6 from upstream of site A5 in Asahikawa River’s mainstream. These outflows might include treated or incomplete wastewaters from ASTSs in densely populated areas with and without centralized sewer systems. Sites T7–T8 are located in residential, commercial, and industrial areas. Both separated (WWTP3) and combined sewer (WWTP2) systems cover almost all areas. They also include unsewered and ASTS areas. In addition, site T7-1 is located in residential, commercial, and industrial areas. Both separated (WWTP3) and decentralized sewer systems cover those areas.

Sewage from areas of combined and separated sewer system for the middle to lower Asahikawa River Basin are treated respectively and are diverted into another watershed. Sewage from the combined sewer system area in the basin is treated mainly at WWTP2. Its effluent is discharged through the

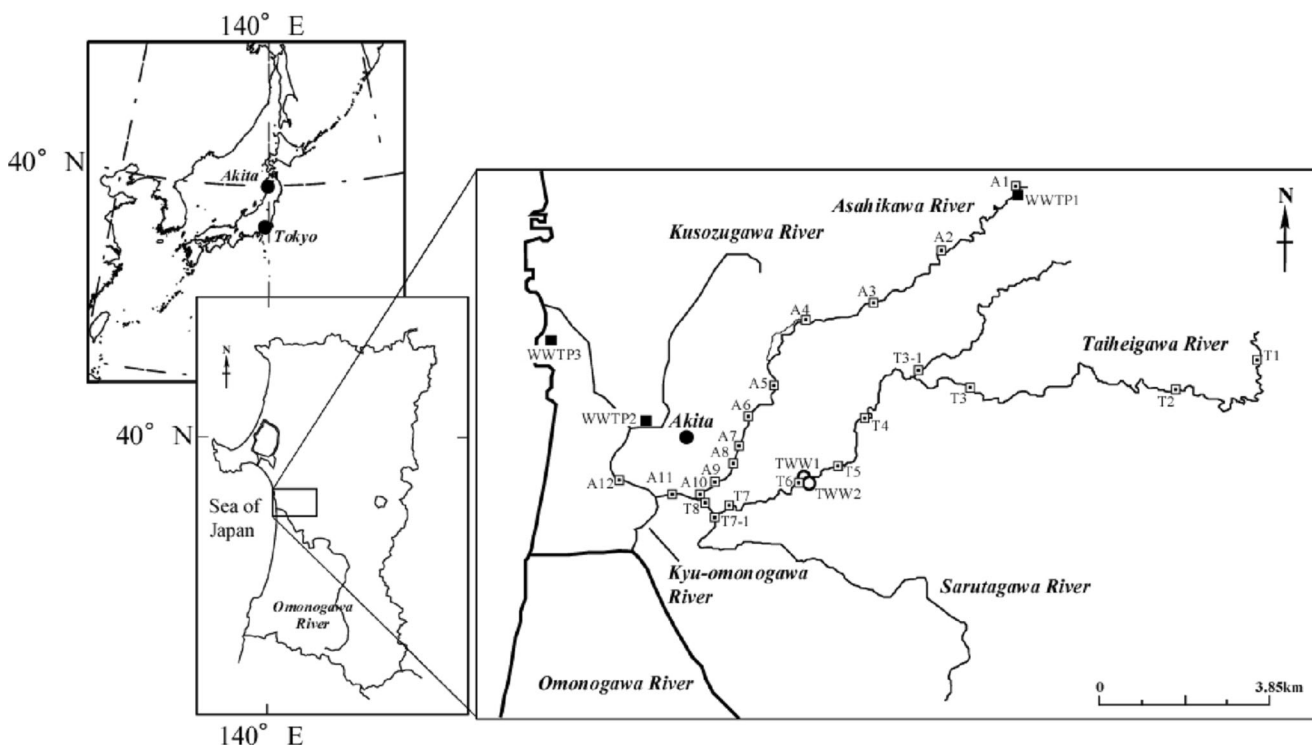


Fig. 1 Sampling locations in Asahikawa River Basin. WWTP1–3, waste water treatment plant; TWW1–2, wastewater outflow point; T1–T8, T3-1, T7-1 and A1–A12, sampling point

lower Kusouzugawa River and into the Akita Canal. Sewage from separated sewer system areas in the middle and lower Asahikawa River Basin is treated at WWTP3; then its effluent is discharged through the Akita Canal into the Sea of Japan.

Sample collection

All samples for this study were collected in the Asahikawa River Basin during winter because the season is regarded as having fewer CSO events as a result of storm water and limited agricultural activity. The area is covered with deep snow. In addition, decreased solar irradiation in winter might reduce abiotic degradation of pharmaceutical compounds (Veach and Bernot 2011). A grab sample of river water was collected from each sampling site of the Taiheigawa River in January 2012 and from each sampling site of the Asahikawa River in February 2012. To confirm the effects of human-use PPCPs from domestic sources for the Taiheigawa River, an additional study was conducted in February 2012. One grab sample of wastewater was collected from agricultural water outflow including treated and incompletely treated wastewater from ASTSs at TWW1 and wastewater from a residential site at TWW2 (both sites near 0.3 km upstream of site T6) in February 2012 for the Taiheigawa River. Each 1-L river water and wastewater sample was collected at these sites. Samples

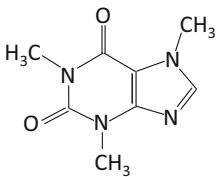
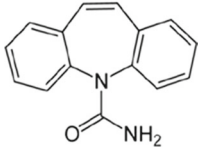
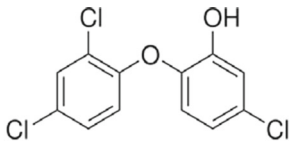
of 0.5–1 L were also collected at each site to assess water quality (total nitrogen, T-N; total phosphorus, T-P; pH; EC; and suspended solids). All samples for this study were kept in the dark at <4 °C until analysis.

Analytical methods

Chemicals and materials

Chemical and physical properties and the predicted no effect concentration (PNEC) for target compounds are presented in Table 1. Target compound standards of caffeine (purity $\geq 98.5\%$), carbamazepine (purity $\geq 98\%$), and triclosan (purity $\geq 97\%$) were purchased from Sigma-Aldrich Corp. LLC. (USA). Respective labeled cleanup internal standards (surrogate compounds) were purchased from Cambridge Isotope Laboratories Inc. (Canada) for $^{13}\text{C}_3$ -caffeine (purity $\geq 99\%$, 100 $\mu\text{g/mL}$), Dr. Ehrenstrofer GmbH (Germany) for d_3 -triclosan (purity $\geq 98\%$, 100 $\mu\text{g/mL}$), and C/D/N Isotopes, Inc. (Japan) for d_{10} -carbamazepine (purity $\geq 98\%$). A GC/MS injection internal standard was purchased (EPA525 Fortification solution B, d_{10} -acenaphthene, d_{10} -phenanthrene, d_{12} -chrysene, and d_{12} -perylene, 500 mg/L each; Supelco, USA). A derivatization reagent of *N*-methyl-*N*-(tert-butyl)dimethylsilyl-

Table 1 Chemical and physical properties, and PNEC for target PPCPs

Compound	Caffeine	Carbamazepine	Triclosan
CAS RN.	58-08-2	298-46-4	3380-34-5
IUPAC name	1,3,7-trimethylpurine-2,6-dione	Benzo[b][1]benzazepine-11-carboxamide	5-chloro-2-(2,4-dichlorophenoxy)phenol
Chemical structure			
Commercial use	Stimulant	Anticonvulsant	Antibacterial, disinfectant
Molecular weight	194.19	236.27	289.54
Water solubility (mg/L)	21,600 ^a	17.7 ^a	10 ^b
LogKow	-0.07 ^a	2.45 ^a	4.76 ^b
PNEC (ng/L)	5,200 ^c	250 ^d	2.8 ^b

CAS RN chemical abstract registry number, IUPAC International Union of Pure and Applied Chemistry, PNEC predicted no effect concentration

^a Kobayashi et al. (2006)

^b Ministry of Environment, Government of Japan (2009.3)

^c Public Works Research Institute, Ministry of Land, Infrastructure and Transport (2012)

^d Komori and Suzuki (2009)

trifluoro-acetamide with 1 % tert-Butylchlorodimethylsilane (MTBSTFA + 1%TBDMCS) was purchased from Supelco.

The target compound standards were prepared with acetone at 1000 mg/L. Their labeled cleanup internal standards were prepared with acetone at 100 mg/L. Then they were prepared with acetone at 1 mg/L. The GC/MS injection internal standard was prepared with acetone at 1 mg/L. Acetone and ethyl acetate were of pesticide residue and PCB-analysis grade (Wako Pure Chemical Industries Ltd., Osaka, Japan). Helium gas and nitrogen gas were respectively of G1 and G2 grade (purity ≥ 99.99995 % and ≥ 99.9998 %; Nippon Sanso Corp., Tokyo, Japan). Ultrapure water was used (arium 611UV; Sartorius, Japan).

Sample preparation and GC/MS analysis

The sample was prepared with HCL (1 + 1) to pH 2 under continuous stirring. Extraction of the target compounds was done using solid-phase extraction apparatus (AQUA Loader Twin; GL Sciences Inc., Japan) with a solid-phase cartridge (Oasis HLB, 200 mg/6 cm³; Waters Corp.). Before extraction, the cartridge was conditioned initially with 10 mL acetone/ethylacetate (1:4, v/v), then with 10 mL acetone, and finally with 20 mL ultrapure water (10 mL \times 2). A labeled cleanup internal standard mixture (¹³C₃-caffeine, d₃-triclosan, and d₁₀-carbamazepine) was added to the extracts before extraction. Regarding the target compounds for Taiheigawa samples, labeled cleanup internal standards were not used because they were unavailable during sample preparation. Then each prepared sample (river water of 1000 mL, wastewater of 20–100 mL) was extracted separately through the conditioned HLB cartridge using the solid-phase extraction apparatus. After the extraction, the cartridges were dried using a centrifuge (10 min/3000 rpm) and a suction manifold with a vacuum pump (30 min). Then, the target compounds were extracted with 10 mL aliquots of acetone/ethylacetate (1:4, v/v) using an elution apparatus (elution pump, Waters Corp.). The extracts were macro-concentrated using a rotary evaporator. Thereafter, they were evaporated to dryness under a gentle stream of nitrogen. Then, they were derivatized with 100 μ L of MTBSTFA + 1%TBDMCS at 40 °C for 90 min with a drying oven. Finally, the labeled GC/MS injection internal standard was added to the derivatized samples.

Analyses by GC/MS were performed using a gas chromatograph (GC)/mass spectrometer (MS) (420GC/320 ms; Bruker Daltonics K.K., Tokyo, Japan) equipped with an automatic sample injector (COMBI-xt; CTC Analytics AG, Switzerland). We achieved GC separation using a capillary column DB5-ms (30 m \times 0.25 mm I.D., 0.25 μ m film thickness; Agilent Technologies Inc., Bellefonte, PA, USA). The GC operating conditions were

the following: 1 min splitless time, injector temperature of 260 °C, column temperature of 50 °C (1 min hold) \rightarrow 20 °C/min \rightarrow 250 °C \rightarrow 5 °C/min \rightarrow 310 °C (5 min hold), helium carrier gas 1.2 mL/min (constant flow), and flow pressure 30 psi at 1 min. The MS conditions were the following: 300 °C ion source temperature, 300 °C interface temperature, electron impact ionization mode, and 70 eV ionization voltage. GC/MS quantitative ions of target compounds and labeled internal compounds were selected from higher intensity peaks. For quantification of the compounds, data acquisition was performed in the SIM mode using the following quantification and qualification ions: *m/z* 194 and 193 for caffeine, *m/z* 193 and 192 for carbamazepine, *m/z* 345 and 347 for triclosan, *m/z* 197 and 196 for ¹³C₃-caffeine, *m/z* 203 and 202 for d₁₀-carbamazepine, *m/z* 348 and 350 for d₃-triclosan, and *m/z* 188 and 94 for d₁₀-phenanthrene.

A series of injections at concentrations of 0, 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 mg/L for mixed target compounds, including the respective 0.05 mg/L of cleanup and injection internal standard, was used to obtain calibration equations. Later, seven-point calibrations were performed over the established concentration range. Linear regression of respective target PPCP peak area/injection internal standard peak areas (d₁₀-phenanthrene only) vs. respective target PPCP concentration/injection internal standard concentration showed good linearity ($R^2 > 0.995$). Data handling was conducted using software (MS Workstation Ver. 7.0, Bruker Daltonics Inc.).

Recovery experiments of the target compounds conducted before performing this study were in the range of 65–107 % (relative standard deviation, RSD 0.6–26 %) for ultrapure water and of 99–113 % (RSD 1.2–14 %) for river water (each sample concentration: 0.02 μ g/L). Recovery results of the target compounds for Asahikawa River samples were in the range of 79–139 % for caffeine, 41–78 % for carbamazepine, and 90–138 % for triclosan. Results obtained from this study were not corrected for recovery. Method detection limits (MDLs) for target compounds were obtained respectively as 4.4 ng/L for caffeine, 0.6 ng/L for carbamazepine, and 1.1 ng/L for triclosan. They were calculated using the standard deviation of operation blank samples ($n = 3$).

Statistical analyses

We analyzed the effects of domestic sewage on the spatial variation of target compounds in the Asahikawa River Basin using cluster analysis. Data shown as not detected (nd) for target compounds were not included in cluster analysis. Furthermore, normalized data for caffeine, triclosan, T-N, and T-P (z-score) were used for cluster analysis. Statistical

analyses were conducted using a computer program (Statistica Advanced; StatSoft Inc.).

Results and discussion

Characteristics of target PPCPs in the Asahikawa River basin

Table 2 presents a comparison of results of target PPCP frequencies of detection and concentrations using data from this study vs. literature data. Caffeine is well known as a chemical that is included in consumer products such as coffee, tea, soft drinks, and pharmaceuticals (Buerge et al. 2003). Caffeine was ubiquitous in the Asahikawa River Basin; it was detected in 92 % of Asahikawa samples and in 100 % of Taiheigawa River samples. Caffeine was as ubiquitous or more ubiquitous than triclosan or carbamazepine. Caffeine has also been reported in Japan and worldwide with high incidence in rivers: Japan, 30–100 %; Asia, 80–100 % (China, 97–100 %; Korea, 80–100 %); EU, 75–100 % (France, Germany, Switzerland, 100 %; Sweden, 75 %); and North America, 52–100 % (Canada, 100 %; USA, 52–100 %) (Table 2). The concentrations of caffeine detected in this study were the highest among the target PPCPs. Caffeine concentrations were detected in the range of <4.4 (nd)–230 ng/L for the Asahikawa River and 4.4–370 ng/L for the Taiheigawa River. The mean and median concentrations were detected respectively as 62 and 47 ng/L for the Asahikawa River and as 150 and 97 ng/L for the Taiheigawa River. These mean concentrations of caffeine were comparable to those reported in Asia, the EU, and North America. These results suggest that caffeine derives from untreated or incompletely treated wastewaters and from high consumption of its related products by people residing in the Asahikawa River Basin. Therefore, caffeine found in this study is a potential indicator of human-use PPCPs for the Asahikawa River Basin. It has been detected in other studies as well (Buerge et al. 2003; Yang et al. 2013; Wu et al. 2014).

Carbamazepine was detected in 100 % of samples from the Asahikawa River and in 70 % of samples from the Taiheigawa River. The frequencies of detection for carbamazepine were comparable to those throughout Japan, but other countries show wider diversity: Japan, 79–100 %; Asia, 50–100 % (China, 50–97 %; India, 100 %; Korea, 67–100 %); EU, 29–100 % (France, 29 %; Romania, 75 %; Spain, 67–100 %; Sweden, 75 %); and North America, 12–100 % (Canada, 100 %; USA, 12–82.5 % (Table 2). The carbamazepine concentration detected in this study was the lowest among the target PPCPs. They were detected in the range of 1.0–3.9 ng/L in the Asahikawa River and <0.6 (nd)–3.5 ng/L in the Taiheigawa River. These mean and median concentrations were detected respectively as 1.6 and 1.3 ng/L in the

Asahikawa River and as 1.8 and 1.8 ng/L in the Taiheigawa River. The concentrations of carbamazepine were clearly lower than those of caffeine: carbamazepine concentrations were 1–2 orders of magnitude lower than caffeine concentrations. The mean concentrations of carbamazepine detected in this study were comparable to those reported for China, India, Canada, and Sweden, but were the same or 1–2 orders of magnitude lower than those in Japan, Korea, France, Romania, Spain, and North America. Regarding antiepileptics such as carbamazepine, they are present in surface water at high–medium nanogram concentration levels (or even at low microgram concentration levels) and are ubiquitous and prevalent; risk is suspected to be high (Hernando et al. 2006). These results of higher detection frequency and lower concentration level for carbamazepine in this study suggest that they might be caused temporarily by changes in consumption and transport processes from its sources. In addition, lower temperatures and decreased solar irradiation in winter will likely only influence the persistence of its compounds (Veach and Bernot 2011).

Triclosan was detected in 75 % of samples from the Asahikawa River and in 70 % of samples from the Taiheigawa River. It was slightly less ubiquitous than caffeine and carbamazepine. Frequencies of triclosan are diverse throughout Japan and respective countries: Japan, 0–100 %; Asia, 0–100 % (China, 0–100 %; India, 100 %; Korea, 0 %); Australia, 90 %; EU, 20–100 % (Germany, 60 %; Romania, 100 %; Spain, 20 %; Sweden, 50 %); and the USA, 0–57.6 % (Table 2). The triclosan concentrations were detected as <1.1(nd)–7.5 ng/L for the Asahikawa River and as nd–13 ng/L for the Taiheigawa River. The triclosan concentrations were comparable to those for carbamazepine. The mean and median concentrations were, respectively, 4.0 and 3.7 ng/L for the Asahikawa River and 7.5 and 3.8 ng/L for the Taiheigawa River. These mean concentrations were 1–2 orders of magnitude lower than those reported in Japan, China, India, Romania, Spain, and the USA. Triclosan has high Kow (octanol–water partition coefficients) yielding maximum potential for particulate sorption relative to caffeine and carbamazepine (Table 1), potentially resulting in higher water column concentrations. However, this study found no clear correlation between triclosan and suspended solids (data not shown). Therefore, these results of lower detection frequency and concentration levels are attributable to the fact that its abundance from wastewater sources (TWW1 and TWW2) to water bodies is low compared with those from caffeine. Additionally, it accumulates in sediments by adsorption partitioning processes in river waters (Veach and Bernot 2011).

Results show that, for the target PPCPs, caffeine is the most suitable indicator to detect sewage pollution clearly in the

Table 2 Results of target PPCP frequency of detection and concentration using data of this study and of the literature

Sampling location	Country	Sampling year	LOD (ng/L)	Frequency (%)	n	Concentration (ng/L)			Literature
						Min–Max	Mean	Median	
Caffeine									
Asahikawa River	Japan	2012	4.4	92	11	<4.4–230	62	47	This study
Taiheigawa River	Japan	2012	4.4	100	10	4.4–370	150	97	This study
Tone River Basin (mainstream)	Japan	2006	50–270 ^a	90	20	b–2100	b	264	Nakada et al. (2007)
Tone River Basin (tributaries)	Japan	2007	0.2	30	14	b–1500	b	420	Ministry of land, infrastructure, transport and tourism (2007)
Tonegawa, Watarasegawa, Kinugawa, Kokaigawa, Edogawa, Nakagawa, Arakawa, Kujigawa, Tamagawa, Turumigawa, Sagamigawa, and Fujigawa River	Japan	2007	13	100	5	860–12,000	5700 ^d	4800 ^d	Komori and Suzuki (2009)
Five tributaries of Ootsugawa River Basin	China	2011	b	97	38	15–865	200 ^d	110 ^d	Yang et al. (2013)
Zhujiang, Shijing, and Beijing River	China	2012	b	100 ^c	16	50.3–786	142	100 ^d	Wu et al. (2014)
Central and lower Yangtze River	China	2005	10	92	12	<10–373	180 ^d	250 ^d	Choi et al. (2008)
Han River	Korea	2004, 2005	10 ^a	100	8	2.9–194	105	b	Kim et al. (2007)
Han, Nakdong, and Youngsan River	Korea	2007	13 ^a	80	5	nd–557	260 ^d	220 ^d	Sim et al. (2010)
Dong Stream, Hakjang Stream, Suyeong, Nakdong, and Meakdo River	France	2004	2.5	100	7	13.0–107.2	50 ^d	25 ^d	Rabiet et al. (2006)
Herault River and its tributaries	Germany	2002	0.25 ^a	100	6	98–150	120 ^d	100 ^d	Weigel et al. (2004)
Elube River	Romania	b	30 ^a	b	b	b,b	428.2–9699.8	b	Moldovan (2006)
Somes River	Romania	2002	b	75	4	<5–110	43 ^d	10 ^d	Bendz et al. (2005)
Höje River	Sweden	2001	2	100	7	26–250	100 ^d	64 ^d	Buerge et al. (2003)
Aabach, Glat, Limmat, Mettlenbach, and Reuss River	Switzerland	2002, 2003	1–15	100	5	23–466	140 ^d	64 ^d	Sosiak and Hebben (2005)
North Saskatchewan, Bow, Oldman, South Saskatchewan, Red Deer River	Canada	2002, 2003	1–15	100	5	23–466	140 ^d	64 ^d	Sosiak and Hebben (2005)
139 stream	USA	1999–2000	14 ^c	61.9 ^c	84	b–6000	b	81	Kolpin et al. (2002)
Miami River	USA	2000	4	100	4	21.8–41.2	30 ^d	28 ^d	Gardinali and X. Zhao (2002)
Miami River	USA	2004, 2006	0.5–1	100	6	13–68	b	b	Singh et al. (2010)
US stream (upstream and downstream samples from WWTPs)	USA	2005	16 ^c	70 ^c	29	b–7990	b	46	Glassmeyer et al. (2005)
Anacostia River	USA	2005–2006	15	78–79 ^c	9	b,b	b	b	Shala and Foster (2010)
Upper White River Watershed	USA	2009–2010	b	96 ^c	25	11–400	b	b	Yeach and Bernot (2011)
Sugar Creek	USA	2010–2011	25.0	52 ^c	8	b–140.0	43.6	b	Bernot et al. (2013)
Carbamazepine									
Asahikawa River	Japan	2012	0.6	100	12	0.7–3.9	1.6	1.3	This study
Taiheigawa River	Japan	2012	0.6	70	7	<0.6–3.5	1.8	1.8	This study
Tone River Basin (mainstream)	Japan	2006	1–3 ^a	80	20	b–12	b	4.5	Nakada et al. (2007)
Tone River Basin (tributaries)	Japan	2004, 2005	0.1	79	14	b–15	b	5.6	Nakada et al. (2008)
37 rivers	Japan	2004, 2005	0.1	92	37	<0.1–34.7	7.3 ^d	3.5 ^d	Ministry of land, infrastructure, transport and tourism (2007)
Tonegawa, Watarasegawa, Kinugawa, Kokaigawa, Edogawa, Nakagawa, Arakawa, Kujigawa, Tamagawa, Turumigawa, Sagamigawa, and Fujigawa River	Japan	2007	0.2	100	14	0.8–51	14 ^d	7.7 ^d	Ministry of land, infrastructure, transport and tourism (2007)
Five tributaries of Ootsugawa River Basin	Japan	2007	0.33	100	5	4.1–91	36 ^d	25 ^d	Komori and Suzuki (2009)
Zhujiang, Shijing, and Beijing River	China	2011	b	97	38	0.2–10	2.6 ^d	2.1 ^d	Yang et al. (2013)
Central and lower Yangtze River	China	2009	1.6	50 ^c	16	nd–2.0	1.1 ^d	1.1 ^d	Wu et al. (2014)
Kaveri, Vellar, and Tamiraparani River	India	2004, 2005	1	100	29	b–5.72–128	b	2.67–13.0	Ramaswamy et al. (2011)
Han, Nakdong, and Youngsan River	Korea	2004, 2005	1	88	8	4.5–61	2.5	b	Kim et al. (2007)
Han River	Korea	2005	5	67	12	<5–36	b	b	Choi et al. (2008)
Mankyung River and its tributaries	Korea	2006	1	80	5	nd–595	230 ^d	140 ^d	Kim et al. (2009)
Dong Stream, Hakjang Stream, Suyeong, Nakdong and Meakdo River	Korea	2007	4 ^a	100	5	12–95	36 ^d	25 ^d	Sim et al. (2010)
Herault River and its tributaries	France	2004	1.4	29	7	nd–56.3	40	b	Rabiet et al. (2006)

Table 2 (continued)

Sampling location	Country	Sampling year	LOD (ng/L)	Frequency (%)	n	Concentration (ng/L)			Literature
						Min–Max	Mean	Median	
Somes River Jarama, Manzanares, Guadarama, Henares, and Tajo River (ca. 100 m downstream of WWTP)	Romania	b	30 ^a	100	4	b _b	<30–75.1	b	Moldovan (2006)
	Spain	2007	10 ^a	67	9	nd–273	110 ^d	82	Alonso et al. (2010)
Ebro River (mainstream)	Spain	2010	<10	100 ^e	b	2.6–11.9	5.93	b	López-Serna et al. (2012)
Höje River (tributaries)	Sweden	2002	b	100 ^e	b	>10–90.4	13.4	b	Bendz et al. (2005)
Höje River	Sweden	2002	b	75	4	<1–0.5	0.35 ^d	b	Miao and Metcalfe (2003)
Otonabee River	Canada	2002	b	b	b	b _b	0.7	b	Sosiak and Hebben (2005)
North Saskatchewan, Bow, Oldman, South Saskatchewan, Red Deer River	Canada	2002, 2003	1–15	100	5	94–206	140 ^d	b	Glassmeyer et al. (2005)
US stream (upstream and downstream samples from WWTPs)	USA	2005	11 ^c	82.5 ^c	29	b _b –270	b	b	Shala and Foster (2010)
Anacostia River	USA	2005–2006	17	48–53 ^c	9	b _b	b	b	Veach and Bernot (2011)
Upper White River Watershed	USA	2009–2010	b	28 ^c	25	1.1–2.7	b	b	Bernot et al. (2013)
Sugar Creek	USA	2010–2011	1.0	12 ^c	8	b _b –8.0	1.1	b	This study
Toriclosan	Japan	2012	1.1	75	9	<1.1–7.5	4.0	3.7	This study
Asahikawa River	Japan	2004, 2005	1.1	70	6	<1.1–13	7.5	3.8	This study
Taiheigawa River	Japan	2004, 2005	0.6	100	37	<0.6–59.1	14 ^d	11 ^d	Nakada et al. (2008)
37 rivers	Japan	2006	b	0–100	9	11–134	b	b	Nishi et al. (2008)
Tone Canal between Tone River and Edo River	Japan	2012	1.1	75	9	<1.1–7.5	4.0	3.7	This study
Five tributaries of Ootsugawa River Basin	China	2007	2.5	100	5	31–360	150 ^d	110 ^d	Komori and Suzuki (2009)
Liuxi, Zhujiang, and Shijing River	China	2007, 2008	1.2	75–100	15	<4.1–478	13.7–242	11.9–238	Zhao et al. (2010)
Central and lower Yangtze River	China	2012, 2013	b	0	16	b _b	b	b	Wu et al. (2014)
Kaveri River, Vellar River, and Taimiraparani River	India	2009	3.0	100	29	b _b –5160	b	8.95–142	Ramaswamy et al. (2011)
Mankyung River and its tributaries ca. 200 m downstream and upstream of five rivers with effluents from WWTPs in Queensland	Korea	2006	10	0	5	nd	b	b	Kim et al. (2009)
Elube River	Australia	2004, 2005	3	90	10	nd–47	b	b	Ying et al. (2007)
Somes River	Germany	2002	0.16 ^a	60	6	nd–4.1	b	b	Weigel et al. (2004)
Liobregat River Basin	Romania	2003–2004	30.0	100	4	b _b	<30–56.7	b	Moldovan (2006)
Höje River	Spain	2002	30.0	20	10	b–45	45	b	Kuster et al. (2008)
139 stream	Sweden	1999–2000	b	50	4	<0.1–70	b	b	Bendz et al. (2005)
Mississippi River	USA	1999–2000	50 ^c	57.6 ^c	85	b _b –2300	b	140	Kolpin et al. (2002)
Miami River	USA	2003	0.2	38	8	nd–3.1	b	<0.2	Boyd et al. (2004)
Anacostia River	USA	2004, 2006	0.5–1	0	6	nd	b	b	Singh et al. (2010)
Upper White River Watershed	USA	2005–2006	10	b	9	b _b –101–248	22–25	b	Shala and Foster (2010)
Sugar Creek	USA	2009–2010	b	12 ^c	25	9.1–22	b	b	Veach and Bernot (2011)
Sugar Creek	USA	2010–2011	2.0	57 ^c	8	b _b –230.0	70.9	b	Bernot et al. (2013)

Frequency = number of detected samples/total number of measured samples (n) × 100(%). The frequency was calculated using data from the literature. HQ = mean concentration/PNEC. PNEC corresponds to those in Table 1

LOD limit of detection, HQ hazard quotient, nd not detected

^a Limit of quantification

^b No data

^c Reporting level or value

^d Mean and median values were calculated using data from the literature

basin, although other PPCP concentrations might rise temporarily according to changes in consumption and transport processes from its sources.

Flux of target PPCPs in the Asahikawa River Basin

To elucidate the contribution of target PPCPs from domestic sewage for the Asahikawa River Basin, their fluxes (g/d) were estimated. Fluxes of target PPCPs at site A10 for the Asahikawa River, at site T7 for the Taiheigawa River, and at site TWW1 (ca. 2.5 km upstream of site T7) of wastewater for the Taiheigawa River were calculated using respective target PPCP concentrations (ng/L) and discharge (m^3/s) during sampling at respective sites. Then their fluxes were compared using those reported results for the Ootsugawa River Basin, which includes a metropolitan area in Japan (Komori and Suzuki 2009), and because the population (ca. 190,000), drainage area (37 km^2), and river length (12.5 km) for the Ootsugawa River Basin were comparable to those of the few reports describing earlier studies.

Fluxes of target PPCPs for the Taiheigawa River were clearly higher than those for the Asahikawa River: 44 and 4.5 g/d for caffeine, 0.82 and 0.43 g/d for carbamazepine, and 1.1 and 0.34 g/d for triclosan. These results of comparison suggest that the contribution to the load for target PPCPs was not attributable to effluents from CSOs for the Asahikawa River but to untreated and incompletely treated effluents from decentralized systems such as ASTSs for the Taiheigawa River. In fact, fluxes of target PPCPs for the Taiheigawa River closely resemble those for the Ootsugawa River Basin, which includes effluents from ASTSs: 44 g/d for caffeine (range 6.9–91 g/d), 0.27 g/d for carbamazepine (range 0.033–0.63 g/d), and 1.6 g/d for triclosan (range 0.25–2.7 g/d) (Komori and Suzuki 2009). In addition, the results were consistent with the fact that wastewater treatment efficiencies of ASTSs are equal to or much lower than those of WWTPs effluents in Japan (Nakada et al. 2007). Furthermore, fluxes of caffeine and triclosan at site TWW1 were respectively and clearly higher than those at site T7: 11 g/d for caffeine and 1.6 g/d for triclosan (carbamazepine was not detected). These results suggest that effluents from site TWW1 are major sources of the lower Taiheigawa River. Higher inputs of PPCPs from ASTSs in an urban area without sewer systems can degrade the water quality of the receiving water body. Accordingly, these results reveal strongly that decreasing PPCP loads from ASTSs are necessary to reduce water pollution by PPCPs in the Asahikawa River Basin.

Spatial variation in concentrations of target PPCPs

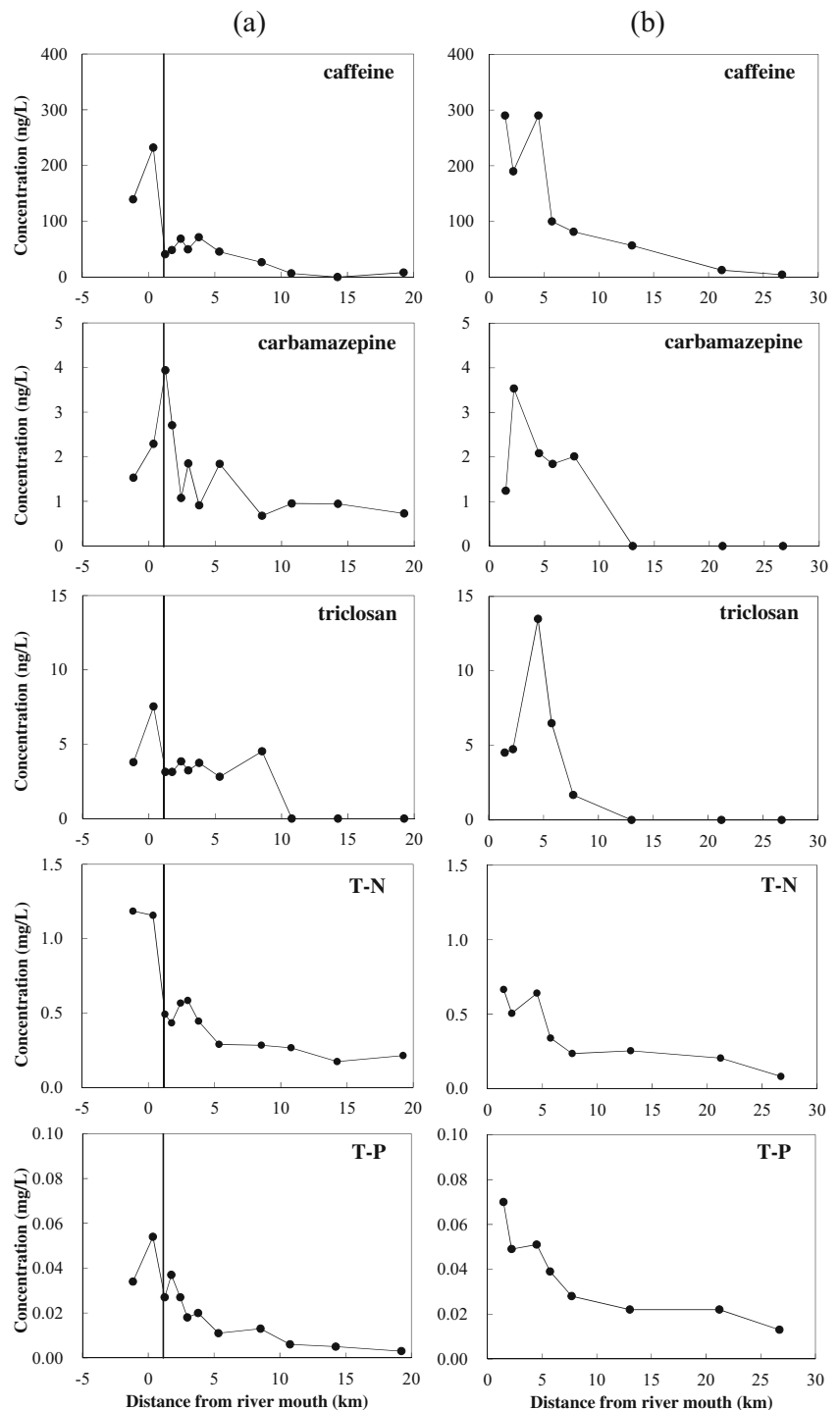
To evaluate the contribution by human-use PPCP sources in the Asahikawa River Basin, spatial variations in target PPCP

concentrations in the mainstream, including T-N and T-P, were examined. Figure 2 presents those results.

Target PPCP concentrations in the upper Asahikawa River Basin (sites A1–A3, ca. >11 km upstream from the Asahikawa River mouth, and at sites T1–T2 >21 km upstream from the Taiheigawa River mouth) were not detected or were markedly lower those in the middle and lower Asahikawa River Basin. Except at site A2, only caffeine was detected at lower and sub-nanogram concentrations for both rivers: nd–8.1 ng/L for the Asahikawa River and 4.4–13 ng/L for the Taiheigawa River. In addition, variations of T-N and T-P concentrations in both upper river basins were similar to those of caffeine. These results demonstrate that caffeine can be a sensitive and adequate indicator along with T-N and T-P, even for less-populated and rural areas in the Asahikawa River Basin.

Target PPCP concentrations in the middle and lower Asahikawa River Basin were detected frequently at lower and higher nanogram concentrations (caffeine, 27–230 ng/L; carbamazepine, 0.7–3.9 ng/L; triclosan, 2.8–7.5 ng/L for the Asahikawa River: sites A4–A12; caffeine, 57–290 ng/L; carbamazepine, nd–3.5 ng/L, triclosan, nd–13 ng/L for the Taiheigawa River: sites T3–T8). Their maximum concentrations were observed at the river mouth or near the river mouth. Regarding Taiheigawa River, higher concentrations for caffeine and triclosan were also observed from its tributary downstream (caffeine 370 ng/L, triclosan, 8.5 g/L for Sarutagawa River: site T7-1). Comparable results for their higher concentrations were observed for T-N and T-P. Previous reports have also described that the spatial variation of target PPCPs in urban areas is generally attributable to input of those higher concentrations from WWTP effluents in the basin (Glassmeyer et al. 2005; Ellis 2006). In addition, Ellis (2006) reported that the WWTP effluent contributes to the dilution of the endogenous concentration of PPCPs already present in the river flow, which reflects a progressive PPCP load with increasing urbanization. However, domestic wastewater effluents from these areas for this study are treated in WWTP2 and WWTP3 and are diverted into other watersheds (Fig. 1). Furthermore, concentrations of caffeine and triclosan in the middle to lower Asahikawa River did not differ from those ca. 1.3–5.3 km downstream of the river mouth (Fig. 2a, caffeine, 41–71 ng/L; triclosan, 2.8–3.8 ng/L), although these sampling sites were situated near several CSO points within a combined sewer system area and although they were included in urban areas of central Akita City. These results might be attributable to the fact that no CSO caused by melted snow was found in CSO points situated along the river during the sampling period used for this study. Therefore, sewage from CSOs in this area might not also be a major potential source in the lower Asahikawa River during winter. These results showing higher PPCP concentrations in the Asahikawa River Basin suggest that diffusion sources such as ASTSs might contribute to the spatial variations of target PPCPs in the basin. However,

Fig. 2 Spatial variation of caffeine, carbamazepine, triclosan, T-N, and T-P concentrations in **a** Asahikawa River and **b** Taiheigawa River. The plot line on the x-axis at ca. 1.1 km in graph **a** shows the confluence of the Asahikawa and Taiheigawa rivers



only the spatial variation of carbamazepine differs; it was increased remarkably in ca. 1.3–2.2 km downstream of the river mouth (Figs. 2a, b, 3.9 ng/L for Asahikawa River, 3.5 ng/L for Taiheigawa River), although caffeine and triclosan concentrations were low or clearly decreased at these sites. Carbamazepine exhibited completely different behavior, suggesting that they might result from changes in consumption and different sources in the lower Asahikawa River Basin.

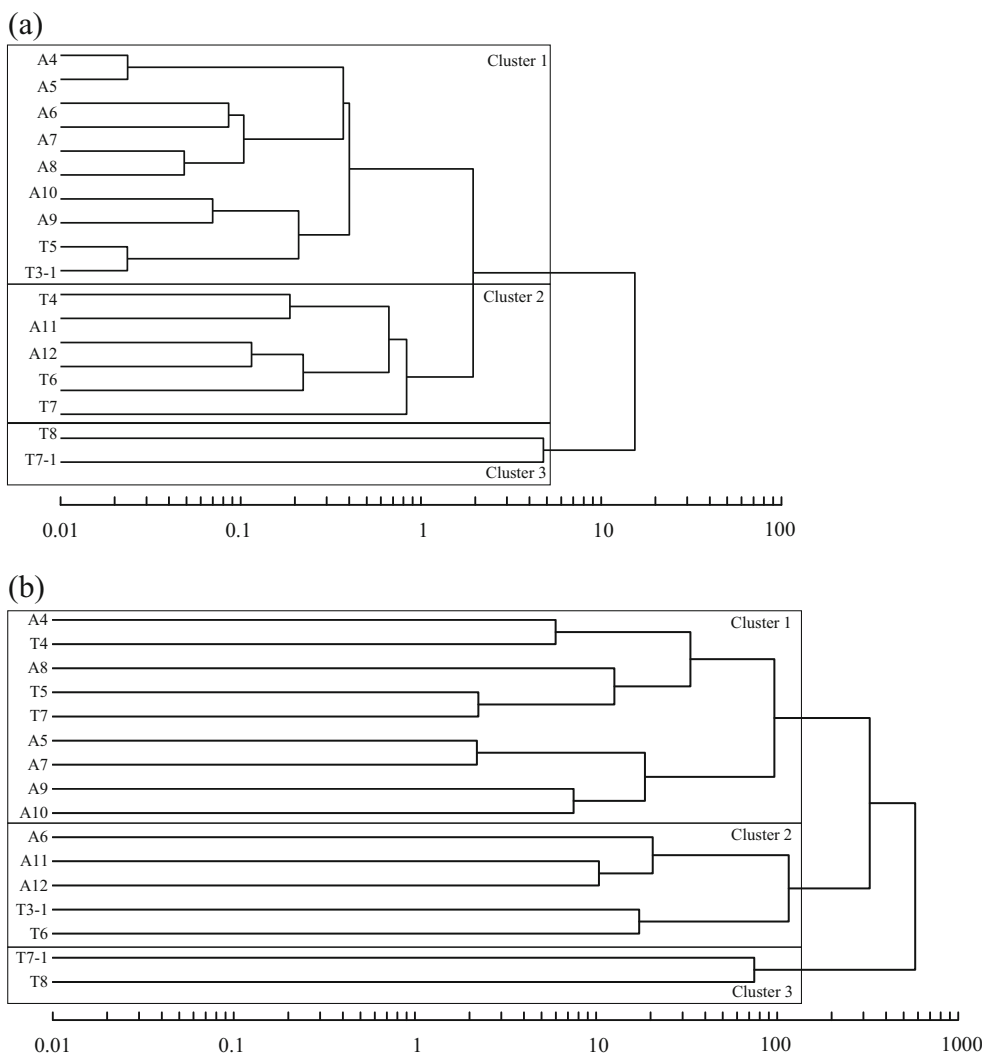
Regarding the wastewater in the Taiheigawa River (TWW1 and TWW2), concentrations of target PPCPs, T-N, and T-P from agricultural water outflows, which might include wastewater effluents from ASTSs in an urban area with and without centralized sewer systems along its stream (TWW1), and ASTS effluents from a residential site (TWW2) at ca. 0.3 km upstream of site T6 were the same or were one order of magnitude higher than those of site T6: TWW1—caffeine,

5700 ng/L; carbamazepine, nd; triclosan, 860 ng/L; TWW2—caffeine, 3600 ng/L; carbamazepine, nd; triclosan, 55 ng/L. In fact, the T-N and T-P concentrations were also one order of magnitude higher than those of river water samples: TWW1—T-N, 6.4 mg/L; T-P, 0.47 mg/L; TWW2—T-N, 4.7 mg/L; T-P, 0.25 mg/L. These results strongly suggest that caffeine and triclosan in wastewater from ASTSs within these areas are attributable to the receiving waters in the Asahikawa River Basin and suggest that carbamazepine might result from changes in consumption in the basin.

Figure 3a presents cluster analysis using concentrations of caffeine, triclosan, T-N, and T-P to clarify the spatial contribution of domestic sewage in the basins. Results of wastewater from TWW1 and TWW2 are included in the cluster analysis. Cluster analysis used to find similarity among the sampling locations produced three clusters for spatial variations of target PPCP concentrations. These clusters were characterized by their spatial proximity and the influence of different sewage effluents. The first cluster mainly included sites located in an urban area with a combined sewer system for the lower

Asahikawa River (sites A6–A10). Results show that the effects of wastewater effluents from sources such as CSOs were weak in comparison to those at downstream sites A11 and A12. In contrast, the second cluster was characterized as sites located in an urban area with combined and separated sewer systems for the lower Taiheigawa River (sites T6–T8 and T7-1), which mainly receive the direct discharge of diffusion sources such as ASTSs in the lower Taiheigawa River, resulting in higher concentrations of target PPCPs. Particularly, higher concentrations of target PPCPs in the lower Taiheigawa River might contribute to those in the lower Asahikawa River (sites A11 and A12). The third clusters might be characterized as sites located in an urban area with a separated sewer system for the lower Taiheigawa River (sites TWW1 and TWW2). However, a comparison of the wastewater effluents for third clusters to waters close downstream (site T6) found them to be significantly different, although the water quality of the lower river basins might be attributable to those of sites TWW1 and TWW2, as described previously. Consequently, cluster analysis for the spatial contribution of

Fig. 3 Dendrogram of sampling sites showing cluster relations. Using **a** concentrations of caffeine, triclosan, T-N, and T-P, and **b** relative molecular indicators and T-P/T-N. Site Nos. correspond to those presented in Fig. 1



target PPCPs is insufficient to elucidate the detection of source-specific domestic sewage pollution caused by ASTSs effluents, even though the spatial contribution of domestic sources in the basins was characterized through analysis. Therefore, further study for the contribution of domestic sources was conducted using relative molecular indicators. Those were described in section 3.4.

Detection of source-specific sewage pollution was conducted using relative molecular indicators in combination with different molecular indicators

Reportedly, carbamazepine, caffeine, and triclosan are well-known potential molecular indicators of sewage in river waters (Glassmeyer et al. 2005). The occurrence and distribution of the molecular indicators in the aquatic environments are generally governed by consumer use patterns, metabolism, excretion, removal rate during wastewater treatment, partitioning (dilution, sorption, and ionization), and degradation (chemical and biological) in respective processes (Jjemba 2006; Lishman et al. 2006). To consider the suitability of target PPCPs as indicators of sewage, we explored their characteristics and behaviors in respective processes before the examination of relative molecular indicators for this study.

Carbamazepine is metabolized to a very high degree in humans. A low proportion of the parent compound is eventually excreted ($\leq 5\%$) (Jjemba 2006). It was removed about 7% consistently across WWTPs, leaving measurable effluent concentrations (Bendz et al. 2005). Additionally, it is generally regarded as moderately hydrophilic (Table 1, Log Kow value of 2.45). It also shows a high degree of persistence in the aquatic environments (Bendz et al. 2005). It appears likely to accumulate in aquatic environments. Therefore, carbamazepine, as a persistent molecular indicator, is useful for tracking the pathways of sewage sources, although carbamazepine is not used as extensively as caffeine. Its concentration in wastewater varies with the community and the period considered (Rabiet et al. 2006).

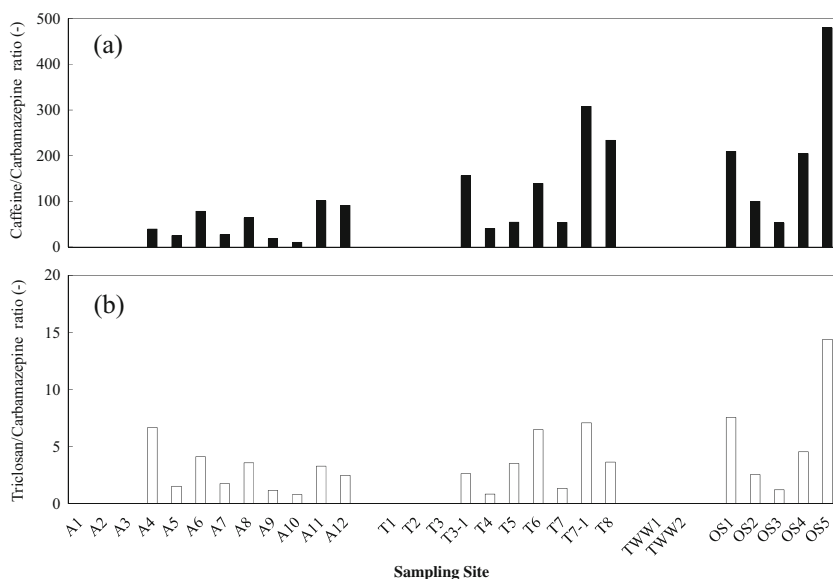
Caffeine is metabolized extensively. Only about 3% of ingested caffeine is excreted unmetabolized in urine and is consistently about >99% removed across WWTPs. However, Seiler et al. (1999) reported that disposal by humans of unconsumed coffee, tea, or soft drinks into the sink can contribute hundreds of milligrams of caffeine to domestic wastewaters. Therefore septic tank effluents can contain ten to hundreds of micrograms per liter of caffeine. Rabiet et al. (2006) also reported that caffeine was detected at a downstream site located far from a WWTP discharge, suggesting that it undergoes no complete degradation either in the WWTP or in the river. Its high consumption might result in detectable inputs of the effluents of the WWTPs. Caffeine's high water solubility and lower Log Kow might also contribute to its high mobility. As a result, higher concentrations make it reasonable

to infer that caffeine is readily present in aquatic environments, although it is a labile compound.

Triclosan is consistently about 55–95% removed across WWTPs (Bendz et al. 2005). In surface waters, it is subject to photolytic transformation with an estimated half-life of less than an hour in natural sunlight (Sabaliunasa et al. 2003). Photodegradation has also been found to be responsible for the rapid removal of triclosan in surface waters in summer (Tixier et al. 2002). However, photodegradation of triclosan for this study might not contribute to the detection in river waters because river water samples were collected in winter. If anything, triclosan has a higher Log Kow of 4.76 (Table 1) among target PPCPs, which might indicate the potential for sorption in sediments and for bioaccumulation in aquatic organisms (Hua et al. 2005). Glassmeyer et al. (2005) reported that triclosan was found in all the WWTP effluent samples in the US streams and reported that downstream concentrations from the WWTPs declined at different rates, with frequencies of detection. Consequently, triclosan might make them candidates for chemical indicators of sewage in river waters. In addition, a bioaccumulation process for antibiotics such as triclosan might be used as an alternative bio-indicator of water pollution and of adverse effects on the sea floor and other aquatic organisms (Richardson et al. 2005). Unfortunately, evaluating the behaviors of triclosan among water, sediments, and aquatic organisms is beyond the scope of this study. Therefore, the discussion of alternative bio-indicators was not included in this study.

Relative molecular indicators, in combination with different molecular indicators of sewage, were also applied to calculation of the contribution of sewage sources in receiving waters (Glassmeyer et al. 2005; Murata et al. 2011). Glassmeyer (2005) reported that, when both compounds have similar persistence in the aquatic environments, their ratios remain fairly consistent in sources and their downstream samples in the basin. However, when concentrations of ephemeral and intermediate compounds such as caffeine and triclosan were compared to those of the persistent compounds such as carbamazepine, a dramatic decrease can be observed in the ratios when the source and downstream ratios are compared. The decrease in the ratios reflects the preferential removal of the less persistent compound in the numerator: ratios of caffeine/carbamazepine and triclosan/carbamazepine for this study might be useful tools to assess the effects of wastewater effluents from sources to near sampling sites in the respective river. Therefore, to assess source-specific sewage pollution in greater detail, relative molecular indicator in combination with different molecular indicators of sewage (ratios of caffeine/carbamazepine and triclosan/carbamazepine) in the Asahikawa River Basin was used for this study. Figure 4 presents the spatial variation of ratios of caffeine/carbamazepine and triclosan/

Fig. 4 Spatial variations of ratios of caffeine/carbamazepine and triclosan/carbamazepine from Asahikawa River (A1–A12), Taiheigawa River (T1–T8), wastewaters for Taiheigawa River (TWW1, TWW2), and Ootsugawa River (OS1–OS5). Ratios for Ootsugawa River were calculated respectively using data from Komori and Suzuki (2009)



carbamazepine for Asahikawa River (A1–A12), Taiheigawa River (T1–T8), wastewater for TWW1 and TWW2, and Ootsugawa River. Unfortunately, ratios of wastewaters for TWW1 and TWW2 cannot be calculated because carbamazepine was “not detected.” Spatial variations of triclosan/carbamazepine and caffeine/carbamazepine ratio (Figs. 4a, b) reveal site characteristics of pollution sources. Regarding caffeine/carbamazepine ratio, sites A6, A8, A11, A12 for Asahikawa River, sites T3-1, T6, T7-1, and T8 for Taiheigawa River, and sites OS1, OS4, and OS5 for Ootsugawa River were higher than those other sites. Regarding the triclosan/carbamazepine ratio, comparable trends were also observed in the respective rivers. Notably, the higher caffeine/carbamazepine and triclosan/carbamazepine ratios for sites T3-1, T6, and T7-1 indicate that treated wastewaters from ASTSs or untreated wastewaters from unsewered system areas are attributable to these areas because ASTS sewer systems cover those areas for sites T3-1, T7-1, and T-6, which have contributions of wastewater from TWW1 and TWW2 for near site T6. Therefore, higher caffeine/carbamazepine and triclosan/carbamazepine ratios in the Asahikawa River Basin suggest that treated or untreated wastewaters from sources can contribute to areas around those sites. In fact, higher caffeine/carbamazepine and triclosan/carbamazepine ratios for OS5 in Ootsugawa River were observed only in the ASTS area (decentralized sewer system area).

Figure 3b presents cluster analysis conducted using relative molecular indicators and T-P/T-N to clarify the spatial contributions of domestic sewage in the basins, as described above. Cluster analysis for relative molecular indicators produced three clear clusters compared to those for molecular indicators, T-N, and T-P (Fig. 3a). These

clusters were characterized by the comparable influence of diffusion sources for ASTSs as described in the previous section. The first cluster mainly included sites located in an urban area with a combined sewer system for the lower Asahikawa River (sites A5, A7, A9, A10) and Taiheigawa River (site T7). They show that the effects of wastewater effluents from sources such as CSOs are weak in comparison to those of downstream sites A11 and A12 for cluster 2. The second cluster of sites A6, A11, A12, T3-1, and T6 for relative molecular indicator characterized as sites mainly receiving the diffusion sources such as ASTSs, resulting in higher relative molecular indicators. Similarly, higher relative molecular indicators in sites A11 and A12 might contribute to ASTSs sources around the sites. The third clusters might be characterized as sites influenced by ASTSs or unsewered system areas from the Sarutagawa River (Fig. 1). It is noteworthy that comparison results of the site T7-1 and T8 for third clusters to site A11 for cluster 2 and of the site A11 for cluster 2 to site A10 for cluster 1 revealed them to be clearly different, although the respective sites were near one another. These results suggest that the contribution of wastewaters from Sarutagawa River to downstream areas is limited, although a maximum or much higher concentration was observed at the site T7-1 compared with the other sites. Although the relative molecular indicators as compared to the molecular indicators can contribute to the detection of sewage, relative molecular indicators are not suitable for the detection in the upper river basin because carbamazepine and triclosan were not detected. Therefore, it is important that detectable molecular indicators such as caffeine and water quality parameters such as T-N and T-P in the upper river basin should be selected to clarify contributions of sewage.

Detection of source-specific sewage pollution using molecular indicators in combination with water quality parameters

Before elucidation of the source-specific domestic sewage pollution using molecular indicators in combination with water quality parameters in the Asahikawa River Basin, we analyzed the relation between concentrations of target PPCPs and water quality concentrations of T-N and T-P in the Asahikawa River Basin. Then, their relations were compared using those reported concentrations for the Ootsugawa River Basin (Komori and Suzuki 2009). Figure 5 presents those results.

Caffeine showed clearly positive correlation with the T-N and T-P concentrations found in the Asahikawa River Basin. The coefficients of determination (R^2) of caffeine and T-N and of caffeine and T-P were, respectively, 0.852 and 0.759 for the Asahikawa River and 0.969 and 0.889 for the Taiheigawa River (Figs. 5a, g). Comparable results for the correlation of caffeine and the T-N or T-P concentration were found for the Ootsugawa River Basin (Figs. 5d, j). Reportedly, comparable results for the

correlation of caffeine and T-N were also found in densely populated areas in China (Wu et al. 2014; Yang et al. 2013). These results suggest that caffeine originates from domestic sewage, with higher positive correlations with T-N and T-P suggesting that their environmental fate (degradation or transformation) in water was similar (Wu et al. 2014). Therefore, relative molecular indicators in combination with their concentrations (ratios of caffeine/T-N and caffeine/T-P) might remain fairly consistent in sources and their downstream samples in the basin, as described in section 3.4. Further examinations for the caffeine/T-N ratio will be described in the following paragraph. Similarly, triclosan showed weak positive correlation with T-N and T-P concentration for the Asahikawa River and with T-N concentration for the Taiheigawa River. The respective R^2 of triclosan and T-N and of triclosan and T-P were 0.517 and 0.691 for the Asahikawa River and 0.589 and 0.420 for the Taiheigawa River (Figs. 5c, i). Comparable results for a positive correlation were obtained using the reported concentrations of triclosan in the Ootsugawa River Basin (Figs. 5f, l). In contrast, carbamazepine showed no correlation with T-N and T-P for the Asahikawa River Basin.

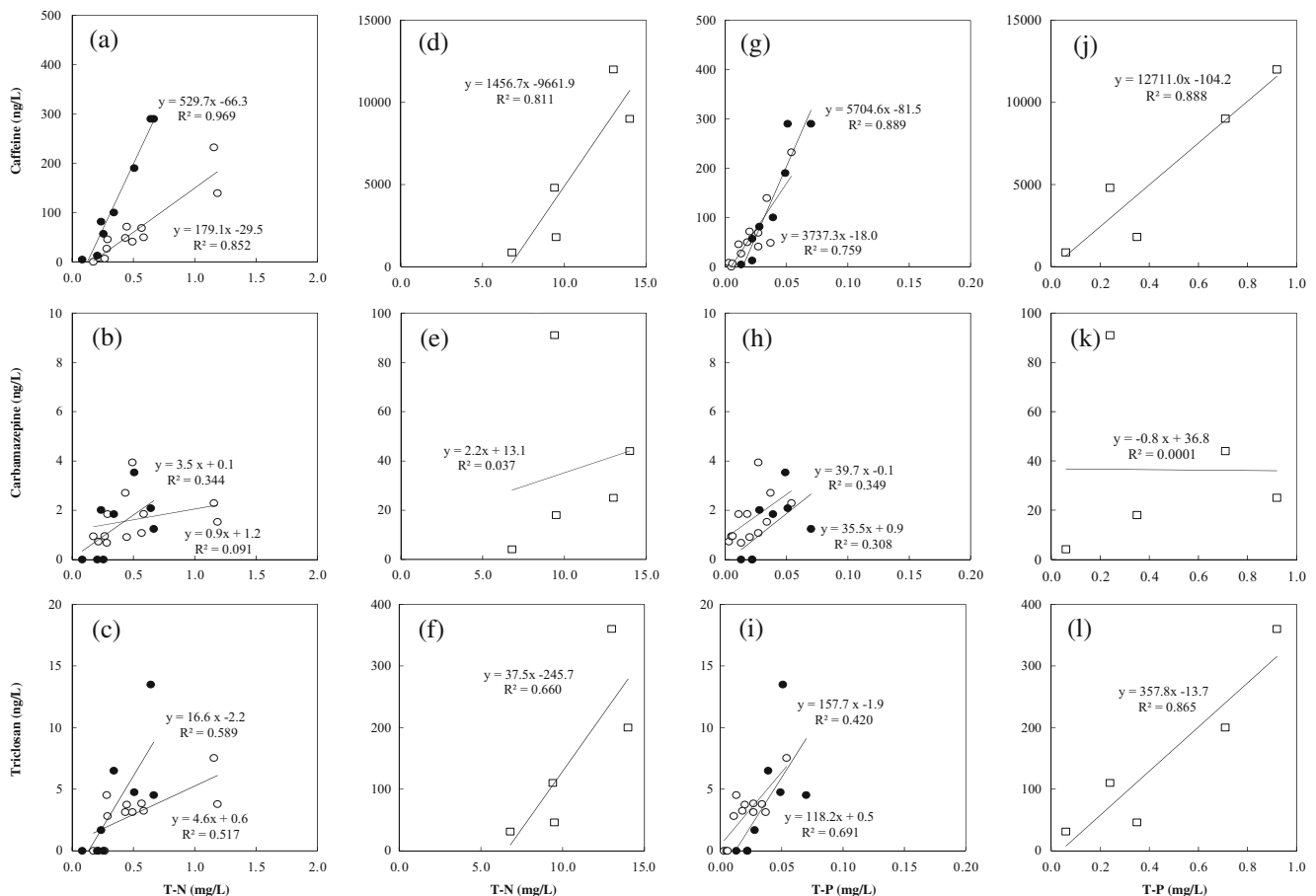


Fig. 5 Relation between water quality (T-N and T-P) and target PPCP concentrations in Asahikawa River (white circle), Taiheigawa River (black circle), and Ootsugawa River (white square). T-N vs. target

PPCPs (a–f), T-P vs. target PPCPs (g–l). Data for Ootsugawa River used in graphs d–f and j–l were referred from Komori and Suzuki (2009)

Respective R^2 of carbamazepine and T-N and of carbamazepine and T-P were 0.091 and 0.308 for the Asahikawa River and 0.344 and 0.349 for the Taihigawa River (Figs. 5b, h). Results indicating no correlation between the molecular indicators were found not only for the Ootsugawa River Basin (Figs. 5e, k) but also for the rivers in China (Wu et al. 2014; Yang et al. 2013). These results suggest that carbamazepine is not used as extensively as caffeine and triclosan, and that its concentration varies with the community and the period considered in river water (Seiler et al. 1999).

To access detection of source-specific sewage pollution using relative molecular indicators in combination with water quality parameters, a comparison was conducted between the caffeine concentration and caffeine/T-N ratio for the Asahikawa River Basin and that for other urban rivers calculated from reported PPCP concentrations in winter (Komori and Suzuki 2009; Wu et al. 2014). Figure 6 presents those results. A higher caffeine/T-N ratio for the Taiheigawa River (ca. $\geq 2.0 \times 10^{-4}$) was observed at sites T3-1-T8, TWW1, and TWW2. Comparable results of the higher caffeine/T-N ratio for the Taiheigawa River were observed at polluted sites OS3-OS5 for the Ootsugawa River Basin. A lower caffeine/T-N ratio (ca. $< 2.0 \times 10^{-4}$) was observed mainly in an urban area with a separated sewer system among sites A6-A10 for the Asahikawa River and at rural areas at sites T1-T2 for the Taiheigawa River. Comparable results of the lower caffeine/T-N ratio were obtained using data reported for the central and lower Yangtze River in China (Fig. 6). However, these were remarkably low compared with data for the Asahikawa River Basin because the nitrogen inputs of both agricultural runoff from the basin and discharge of treated or untreated municipal wastewater from urban areas along the river were also included in the T-N concentrations. Exceptionally, caffeine/T-N ratios at site C13 for Yangtze River were remarkably higher than those at other sites because of the area's higher municipal

wastewater loading from a large city with a larger population (6.0×10^{-4}). Furthermore, comparable results for caffeine/T-N ratio were obtained for the caffeine/T-P ratio for Ootsugawa River, except for site OS1 (data not shown). These results of comparisons suggest that the difference in the contribution of sewage from domestic sources is consistent with trends of the ratios of caffeine/T-N and caffeine/T-P. In fact, sewered populations of sewage at polluted sites (OS3-OS5) for the Ootsugawa River Basin were remarkably lower than those at less polluted sites (OS1-OS2).

Figure 6 also shows the variation of caffeine concentration in Asahikawa River Basin. It was consistent with the trend of the caffeine/T-N ratio. A comparable trend of the caffeine/T-P ratio was observed (Data not shown). However, concentration levels of caffeine in both Taiheigawa and Asahikawa River closely resemble each other, although the flux of caffeine for the Taiheigawa River is clearly higher than that for the Asahikawa River, as described in section 3.2. In addition, the caffeine/T-N ratio showed positive correlation with flux in river waters from Asahikawa River Basin (site A10 and T7 for this study) and Ootsugawa River Basin (OS1-OS5) (Fig. 7). These results suggest that the caffeine concentration alone as a molecular indicator is insufficient to reflect differences in the spatial contributions of domestic sources for human-use PPCPs for urban areas. Therefore, the caffeine/T-N ratio can be a useful and clear indicator representing differences in the contributions of domestic sources for human-use PPCPs in urban areas without sewer systems. A previous study also demonstrated that caffeine measurements in rivers indicate the presence of wastewater directly and sensitively, and that they are more suited for quantitative, integrative assessment of the wastewater burden on surface water in a region (Buerge et al. 2003). Results of the present case study of the Asahikawa River Basin also support the suggestion presented above, but the caffeine/T-N ratio does so more clearly and quantitatively than the caffeine concentration. Moreover,

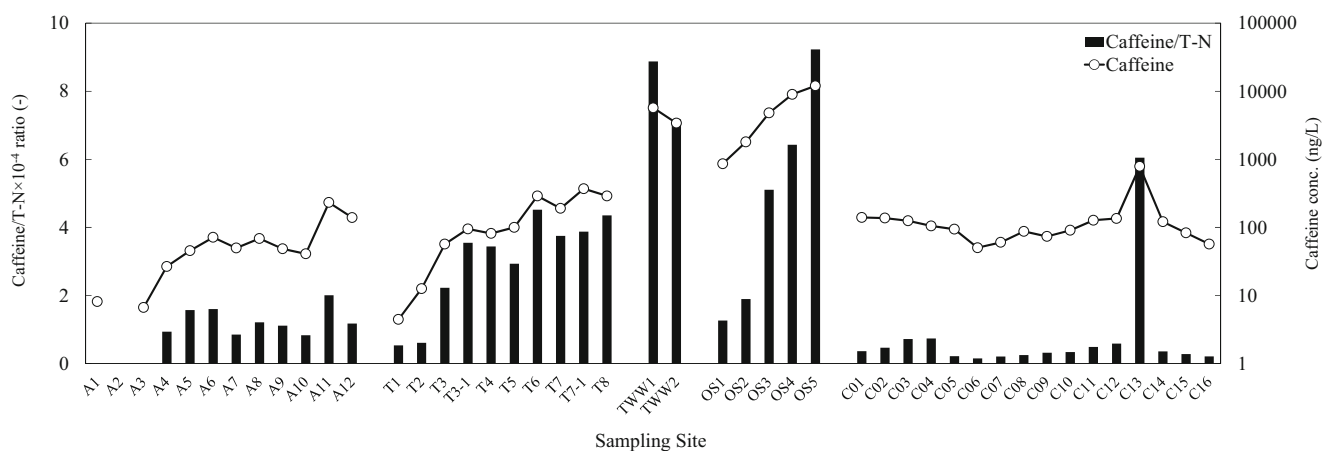


Fig. 6 Comparison results of caffeine/T-N ratio from Asahikawa River (A1-A12), Taiheigawa River (T1-T8), wastewaters for Taiheigawa River (TWW1, TWW2), Ootsugawa River (OS1-OS5), and Yangtze River

(C01-C16). Ratios for Ootsugawa River and Yangtze River (central and lower) were calculated respectively using data from Komori and Suzuki (2009) and Wu et al. (2014)

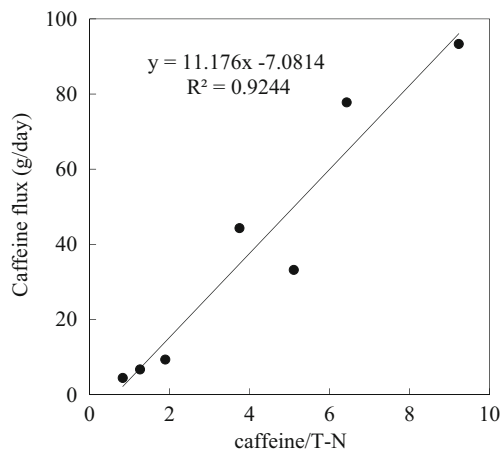


Fig. 7 Relation between caffeine/T-N ratio and caffeine flux in river waters from Asahikawa River Basin and Ootsugawa River Basin was calculated respectively using data from Komori and Suzuki (2009)

the ratio reflects variations of caffeine flux from effluent sources, although respective caffeine and T-N concentrations might not be susceptible to such variations.

Conclusions

Results obtained from this study indicate caffeine as a suitable molecular indicator of domestic sewage in the basin: it was detected ubiquitously and at higher concentrations among target PPCPs. It has been detected in other studies as well. The higher caffeine and triclosan concentrations detected in wastewater effluents and a strongly positive mutual linear correlation between caffeine and either T-N or T-P ($R^2 > 0.759$) reflect the spatial contribution of ASTS effluents in the lower Taiheigawa River. Molecular indicators and their relative molecular indicators in combination with different molecular indicators (ratios of caffeine/carbamazepine and triclosan/carbamazepine) can contribute to sewage detection in the basin. Relative molecular indicators in combination with water quality parameters such as caffeine/T-N can also contribute to sewage detection in the river waters. Particularly, caffeine/T-N does so more clearly and quantitatively than the caffeine concentration. Not only the caffeine concentration, caffeine/carbamazepine, and triclosan/carbamazepine, but also the ratio of caffeine/T-N can be a useful and clear indicator representing differences in the contributions of domestic sources for human-use PPCPs without sewer system areas in the basin. Particularly, a benefit of using caffeine/T-N is that it reflects variations of caffeine flux from domestic sources, although respective caffeine and T-N concentrations might not be susceptible to such variations. The ratio of caffeine/T-N found in this study can also be a useful indicator of the difference in spatial contributions of domestic sewage for human-use PPCPs in urban areas.

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