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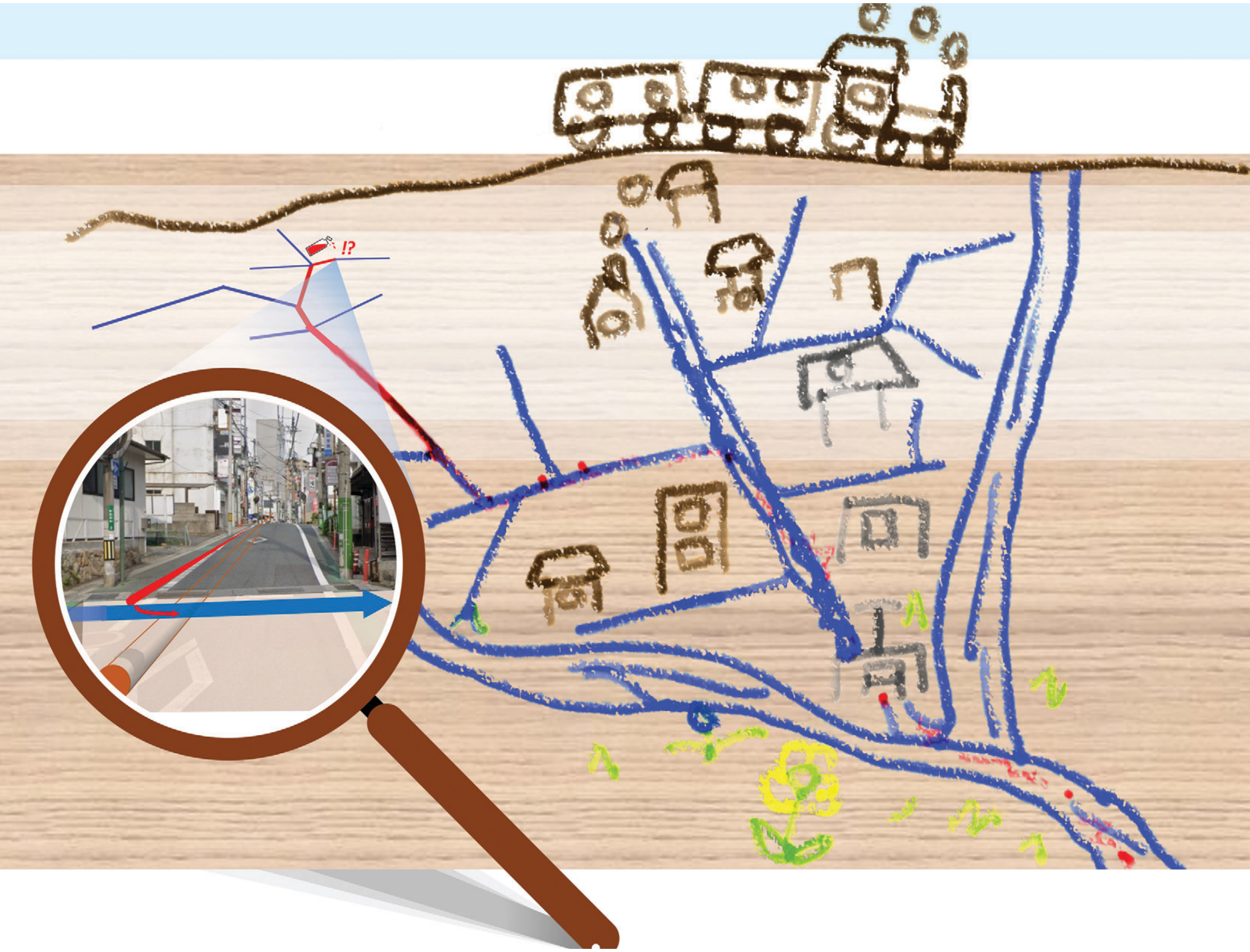

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Detection of domestic-use chemicals in urban storm drains during dry days in a separated sewer area†

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The decrepitude of infrastructures currently threatens developed countries, including Japan. Thus, the development of effective management and maintenance techniques is important. In this respect, the leakage and destruction of separated domestic sewer pipelines are worsening in urban areas because of poor maintenance, as they have existed for over 60 years. Even minor cracks could cause sewer leakage and severe potential subsurface and surface water pollution. Thus, in order to examine the urban stormwater pollution due to leakages of domestic sewers in urban areas, the concentrations of domestic-use chemicals (fragrance compounds) and polycyclic aromatic hydrocarbons (PAHs) were measured in storm drains on no-rain days in an urban watershed area with old separated sewers developed over 40 years back. From the measurements, the concentrations of the domestic-use chemicals were higher at the final outlet of the storm drain than those in rainfall and puddle waters. On the other hand, the PAH concentration was similar to or higher for rainfall and puddle waters. The high concentration of the domestic-use chemicals in the discharge was mostly attributed to chemical inputs during subsurface water transfers, rather than solid/liquid/air partition changes. By measuring concentrations in the storm drain networks in the area, two hot spots were found. One was suggested to be from direct discharge from a household, and the other could be due to double misconnection from one or more households (unrevealed) to a vestige of an old sewer pipeline and from the vestige to a storm pipeline. The stable high concentration at the final discharge was suggested to be due to the loading from these hot spots. The study pointed out the possibility of leakages of domestic sewages due to poor maintenance in old domestic sewer networks, which can increase the risks for public health and indicated the effectiveness of fragrance compounds as tracers for the leakages.

Water impact

A field research technique for finding the leakage from decrepit sewer pipelines into urban water areas has been demonstrated. A possible leakage was found by this methodology in the central district in an urban area, using fragrance substances as a tracer. While the tracers used in this study were found to be applicable, the background level, *i.e.*, the rain input also proved to be nonnegligible.

Introduction

In urban areas with separated sewers, domestic wastewater is separated from rain drainage and is designed not to directly flow out to urban water areas with rainfall. However, because of improper management such as connection mistakes, poor maintenance, or deterioration of pipelines, rainwater and/or groundwater inflow or infiltrate into domestic sewer systems or, adversely, domestic wastewater leaks to urban water areas, including subsurface water systems.[1–3] Furthermore, in worst cases, pipes can collapse with covering road pavements, which may cause severe traffic accidents or even human injury. Besides these worst cases, the leakage of domestic wastewater into water areas can cause water pollution or pathogenic public health risks. For many urban areas, it has been a long time since sewer pipelines were first developed. Moreover, even for separated sewer systems, more than 50 years have passed for the most neglected pipelines since they were first constructed in developed countries such as Japan. Hence, nowadays, the decrepitude and renewal of such

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infrastructures have become important issues for such countries.

Leaks from sewer pipelines may pollute urban groundwater and surface water. In these cases, storm pipelines would be important paths for the transfer of such pollutants because storm discharge networks are sometimes even older than sewer pipelines.[4] Sewage leakage would vary greatly by location, and effective diagnosis is difficult because the leakage is ordinarily hidden in subsurface layers and just a point or line (one-dimensional) probing is available for at least the two-dimensional distribution under subsurface layers. In this regard, various diagnostic methods have been developed (Panasiuk *et al.*[4] [stormwater]; De Silva *et al.*;[5] Rutsch[6] [groundwater]), such as direct eye (or camera) observation, spot leakage measurements, sewer condition monitoring, and tracer spiking testing. Estimates for leak ratios sometimes vary up to thousands of times,[7,8] possibly reflecting the spatial diversions in subsurface layers, and the long history differences in developing the sewer networks. Studies confirming such influences are limited, and their methodologies have not been well developed,[9,10] despite the leakage situation being expected to be rather diverse. The applicable detection technique would, by necessity, be common regardless of the situations when in fact, different application techniques should be considered for different situations.

There have been several studies evaluating the contribution of domestic wastewater contamination in storm drains and surface water.[11–18] They have two different areas of focus: to examine the contamination level of the surface water for a wide spatial range, and to find the specific leakage points. Tracers for detection are classified as bacterial and chemical analysis. For chemical analysis, Buerge *et al.*[11] chose caffeine as a tracer, and the concentrations in rivers in urban to rural areas and lakes were measured in Switzerland. The concentrations ranged from 6–250 ng L^{-1}, and from a mass-balance analysis, the authors concluded that more than half of the caffeine would come from untreated domestic wastewater. Sankararamakrishnan and Guo[12] measured fecal coliforms and caffeine in storm drains in an urban residential area facing a small lake in New Jersey, USA, and found that both contaminants were high in a storm drainage during rainfall events (fecal coliforms: 5000 − >160 000 MPN/100 mL, caffeine: 45 000 ± 3000 ng L^{-1}). Sauvé *et al.*[13] measured caffeine concentrations of the discharges after rainfalls in small streams, brooks, collectors and storm sewer outfall pipes from a stormwater system in a residential area in Montreal, Canada. The concentrations were up to 10^4 ng L^{-1} with a high correlation with *E. coli*, suggesting the influence of domestic wastewater runoff observation by high caffeine concentration. Carbamazepine was also measured as a tracer, but no correlation with *E. coli* was obtained. Yin *et al.*[14] analyzed storm drainage during dry periods at a residential area in Shanghai, China, with acesulfame and theanine as markers of domestic wastewater, which were chosen from 52 chemical species as candidates from their precedented pollution source analysis. Their detected concentrations were up to 10^4 ng L^{-1} in order, and the authors claimed this would be due to the inappropriate inflow of domestic wastewater. Turning further to studies on groundwater pollutions, we find that in addition to caffeine, carbamazepine, and acesulfame,[2,19,20] amidotrizoic acid[2] and HHCB[20] have been applied as successful chemical tracers of domestic wastewater contamination. However, the number of studies are limited, and background effects such as rainwater have yet to be fully discussed.

The purpose of this study is to explore the leakage situation of domestic sewers in an urban separated sewer area having an aged separate sewer and storm drain network. To determine this, the extent of micropollutant discharges thought to be derived from domestic wastewater was investigated in the baseflow of the storm drain during no-rainfall periods, and the source of the discharges was explored. The target area is a district where a separate sewer system had been developed dating back to 40 years. Artificially synthesized fragrance substances, which are stably detected in urban domestic sewers worldwide, were chosen as a tracer of the domestic sewage. Polycyclic aromatic hydrocarbons (PAHs) were also introduced as reference substances. These substances have been included in major non-point pollutants from urban areas, such as vehicle exhaust, asphalt and tire debris, roof linings.[21] Their introduction enables a comparison of the sources and paths with the tracers, as the pollution sources and the paths are considered to be different.

For the first step, the concentration of the fragrance substances was measured for the water flowing from the most downstream storm drain of a rain outflow basin during dry periods in an urban area with a separated domestic wastewater system. In the studied area, water steadily flowed from the storm drain even on dry days, albeit in small amounts. For the second step, following the observation of the stable higher concentration in the first step, the distribution of running water or standing water in storm drainages in the area was measured during no-rainfall periods, and the hot spots were explored. Their emission source was inferred from further field surveillance around the determined hot spot areas. Based on the measurements, the possibility of discharge of domestic wastewater into water bodies, its sources and impacts, and the validity of the methodology of this study were discussed.

Materials and methods

Description of the storm drainage area

The study area is a storm drainage area in the central district of Higashi-Hiroshima City, located 20 km east of Hiroshima City, southwestern Japan (Fig. 1). This area is in the city center area of the city, of which the population is approximately 200 000. The land use of the area is a mixture of historic, business, commercial, and residential districts.

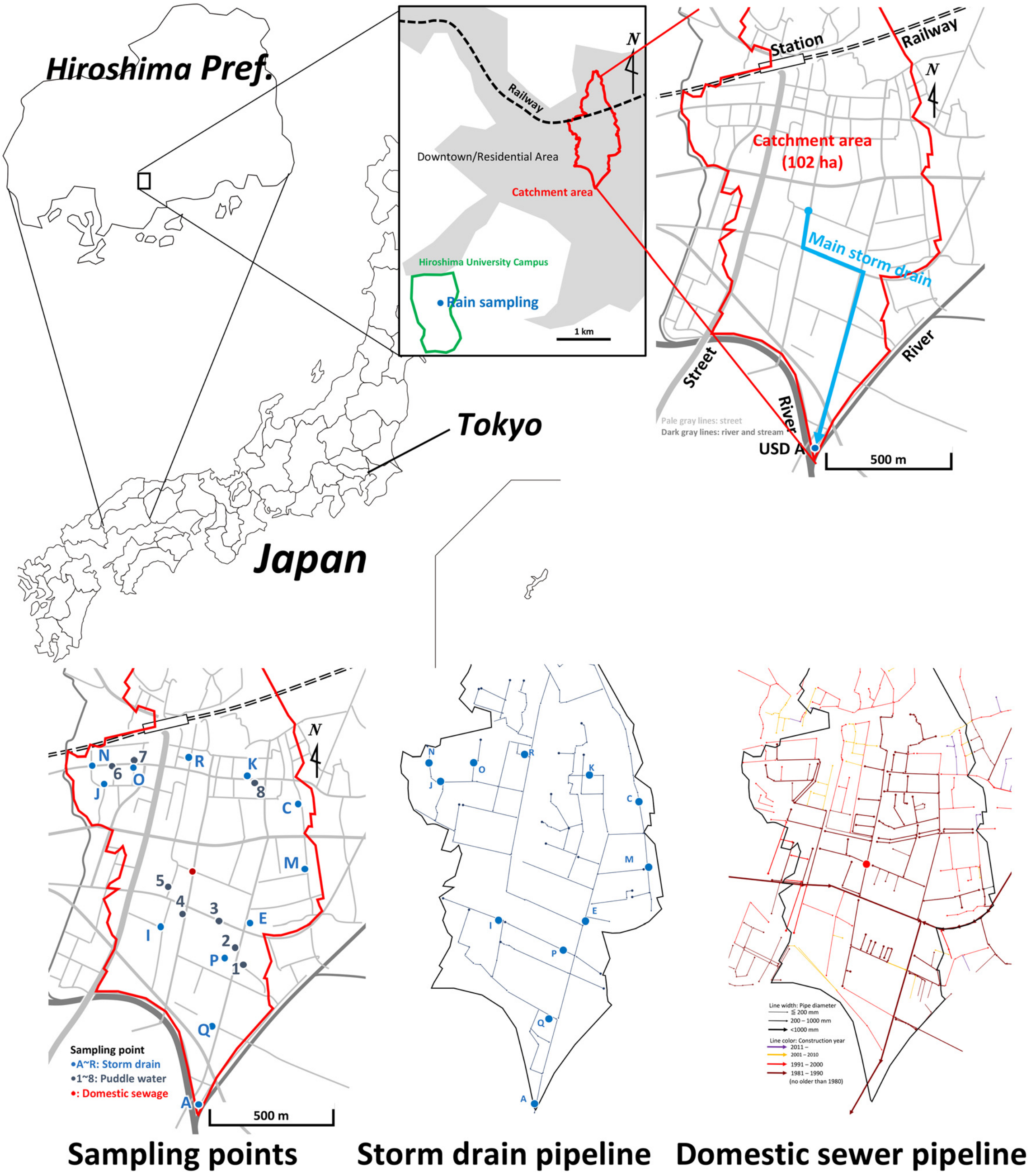


Fig. 1 Map of storm drainage area.

The storm water was collected and drained at a major storm drain outlet (urban storm drain [USD] A; Fig. 1). All storm surface drains were designed to concentrate in this outlet. This major line (blue line on the figure) was constructed (in 2018) to prevent flooding during intense rainfall. Other storm drain pipelines were fairly old, dating back to 40 years. The domestic sewer pipelines were also fairly old, date back to 40 years at the oldest (see "Domestic sewer pipeline" in Fig. 1). The watershed area is 103 ha and is home to 6000 people (population density: 59 person ha^{-1}). The yearly precipitation is 1200–1800 mm year^{-1}. The sewage coverage is almost 100% with several exceptions, and sewage is conveyed to a sewage treatment plant by sewer pipelines, which are separate from the storm drainage.

Sampling

The sampling campaign was divided into two stages. In the first stage, samples were collected from the storm drain outlet, and domestic sewages and rainfalls (direct collection and puddle water) were collected for reference and background, respectively (Table 1). The storm drain was collected 11 times from the stormwater outlet (USD A) during no-rainfall periods (Fig. S1†). Meanwhile, domestic sewage

Table 1 Sampling campaign (for both first and second stages)

Sample name	Number
Rainwater	10
Puddle water	15
Urban storm drain water (USD A)	11
Urban storm drains	30 (12 points)
Domestic sewage	4

was collected four times directly from a sewer pipe at a point in the downtown area (Fig. 1). The aerial coverage of the collection of the sewage at the point is approximately one-fifth in the area. These waters were collected during no-rainfall times more than 48 h after the last rainfall ended. The rainwaters were collected in Hiroshima University campus, which is located 4 km away from the area (Fig. 1). The water was collected using a stainless tray and a bottle. The collection items were set up on noticing the rainfall; consequently, the collected rainwaters did not necessarily contain the first flush. The puddle waters were collected at a point on a roadside in the area (point 1 in "Sampling points" in Fig. 1). Additionally, in order to check a possible field variation of puddle waters, puddle water samplings were conducted in eight sampling points in a rainfall time at a day (2022/11/23 13 : 45–14 : 45, at points 1 to 8). The rainfall and puddle sample collection were limited to just once for a rainfall event, respectively. All samples were collected from May 2021 to December 2021 for storm drains, to July 2022 for rainwater, and to November 2022 for puddle water.

In the second stage, the storm drain water samplings were conducted in the catchment area during no-rain periods. Standing residue waters were collected from storm drain pitches during no-rainfall periods. All these waters were collected from the area shown in "Storm drain pipeline" in Fig. 1, and at a time more than 48 h after the last rainfall ended. Samplings were conducted one to seven times for each rainfall event interval. Characterizing the sampling point, the northern part is a historical area (points N, J, R, K, and C). The southern part is a comparably newer residential and commercial area (points M, E, I, P, and Q), though not simply divided. Some pipelines are in the vicinity of the older sewer pipelines (N, J, R, and K; see "Domestic sewer pipeline" in Fig. 1). For N and J, the storm drain also seemed to be older (Picture of points J, N, and Q are shown in Fig. S1†).

For the analysis, 0.2–2 L of water samples were collected. Thereafter, the concentrations of suspended solids (SSs; filtered using a glass-fiber filter with a cutoff pore size of 0.7 μm) and the targeted micropollutant concentrations were measured for both SS (particulate) and dissolved phases. The targeted compounds were classified as domestic-use chemicals and PAHs. For domestic-use chemicals, five fragrance compounds (FCs) were targeted: 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5*H*)-indanone (known as cashmeran), (1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalene-2yl) ethan-1-one (known as iso-E-super), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran (known as galaxolide), 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone (known as tonalide), and musk ketone 4′-*tert*-butyl-2′,6′-dimethyl-3′,5′-dinitroacetophenone. For the PAHs, three species were targeted: phenanthrene, fluoranthene, and pyrene. These FCs are frequently detected in high concentrations in domestic wastewaters in many countries, including the United States, European countries, and Japan,[22–33] and are thus expected to be effective tracers. For conventional water quality indices, SS and dissolved organic carbon (DOC) concentrations were measured.

Pretreatment

Each water sample was filtered through a 0.7 μm glass-fiber filter (GF/F; Whatman Co. Ltd.), and the filter was dried for 2 days at room temperature in a desiccator in the dark. The filtrate was percolated through a silica column cartridge (Sep-Pak Plus tC18, Waters Co.) at a flow rate of 1 mL min^{-1} and dried with airflow for 2 h. The filtered sample was extracted using 10 mL of dichloromethane (DCM) in an ultrasonic water bath. The column was eluted with 10 mL of DCM at a flow rate of 1 mL min^{-1}. Both DCM extracts were concentrated into 100 μL with a gentle stream of nitrogen gas. The laboratory processing commenced within 2 h after sampling. Before use, the laboratory glassware was cleaned with DCM and heated to 100 °C for 24 h or 600 °C for 4 h for glass vials. The glass fibers were heated to 100 °C for 24 h. The silica cartridge was preconditioned using 100 mL of methanol at a flow rate of 3 mL min^{-1}, and cleaned with 100 mL of pure water at the same flow rate.

Mixtures of benzophenone-d10, phenanthrene-d10, and chrysene-d12 were applied as internal standards for the correction of the gas chromatography/mass spectrometry (GC/MS) peak detection sensitivity for the five FCs, phenanthrene, and both fluoranthene and pyrene, respectively.

Instrumental analysis

The compounds' concentrations were analyzed using a gas chromatograph equipped with a mass spectrometer (GC-17A/MS-QP5050A; Shimadzu Co.) operated in the single-ion monitoring mode. The injection was 1 μL in volume and was split with the detector, and the inlet temperature was set to 300 °C. The initial temperature was 130 °C, which was held for 2 min. The samples were then heated at 30 °C min^{-1} to 210 °C, at 5 °C min^{-1} to 295 °C, and at 2 °C min^{-1} to 315 °C with 10 mL min^{-1} He as the carrier gas. The mass transfer line and ion source were held at 300 °C.

Quality control

The detection limit was set at the level of 3 for the signal-to-noise ratio. The instrument detection limits ranged from 0.7 to 7 pg for each species. Within this level, the coefficient of variation of each compound was less than 20%. The extraction quality was checked through spike recovery testing for dissolved phases, and the recovery ratio was 80–110% for each species. The solid-phase extraction was checked using a dried marine sediment sample certified for PAHs (HS-3B, National Research Council of Canada Institute for Marine Biosciences). The recovery averaged 50–80%, and the repetition error was 5–10%. During the sampling campaigns, a traveling blank was occasionally processed (five times). The concentrations of the targeted compounds were below the detection limits.

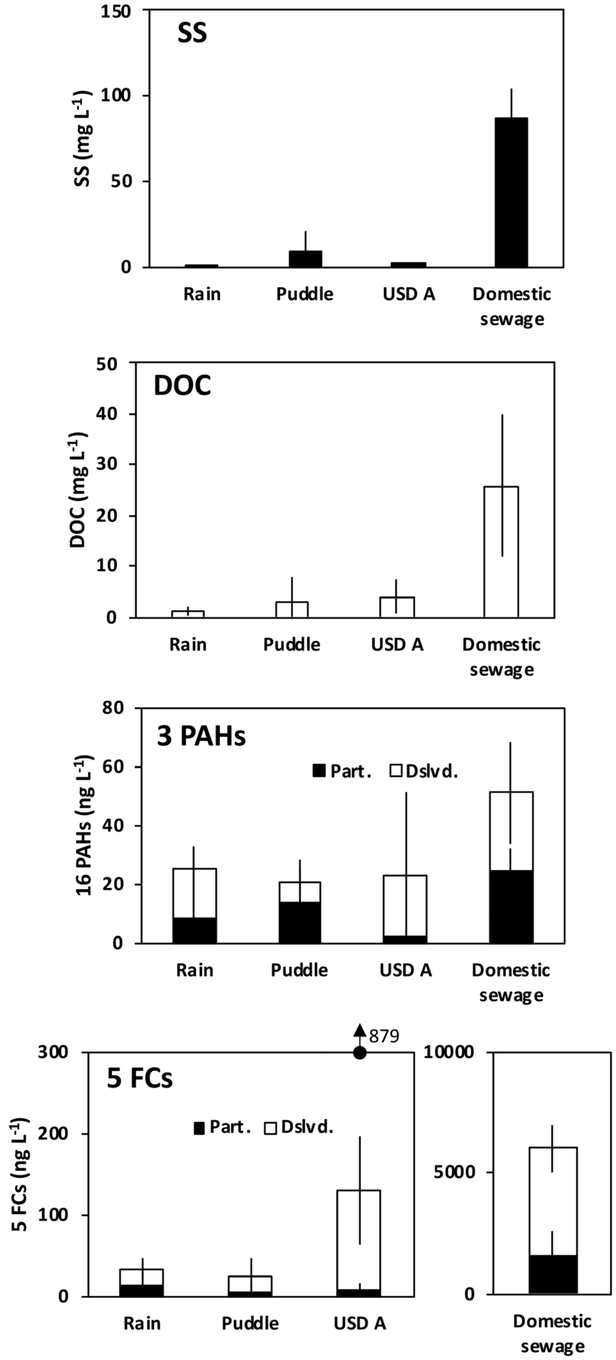


Fig. 2 SS, DOC, targeted compounds concentrations (mean ± sd).

Results and discussions

Comparison of different field stages

The levels of conventional tracers (SS and DOC), the sum of the five FCs, and the sum of three-PAH species were summarized for each field stage (rain, puddle, USD A, and domestic sewage) (Fig. 2; date series of sampling are shown for rain, puddle, and USD in Fig. S1†). The highest concentrations were commonly observed for the domestic sewage for all items. For domestic wastewater, water quality is measured officially in Japan as the influent of every wastewater treatment plant. The nationwide average for SS can be calculated from Japan's official yearbook of the sewer system as 170 ± 88 mg L^{-1} (mean ± sd; FY2019), which was comparable with our results. Although the total organic carbon (TOC) or DOC was not measured regularly, potassium permanganate oxidation (COD_{Mn}) was periodically measured, which is considered similar to TOC as an organic substance index if the pollutants are primarily composed of organic substances. If they are represented as $(CH_2O)_n$, the value can be converted to 40 ± 18 mg L^{-1} using the molar weight ratio of C/O_2 as 12/32. This converted value is also comparable with our DOC value. The levels of the three PAHs and five FCs for the domestic sewage were 51 ± 23 ng L^{-1} and 6002 ± 822 ng L^{-1}, respectively.

Musk compounds and PAHs have been extensively measured in domestic wastewater in various studies, such as our previous measurements at the inlet of a wastewater treatment plant for the area including this watershed.[33,34] The concentrations of each PAH species were in the order of tens to thousands of ng L^{-1},[35–42] whereas those of the musk compounds were in the order of several thousands to tens of thousands of ng L^{-1}.[43] Our results for domestic wastewater were comparable to these values.

The rainwater concentration and puddle water concentration were 35 ± 18 ng L^{-1} and 27 ± 25 ng L^{-1}, respectively. Both were comparable, indicating that the surface concentration level primarily reflected the rainfall loading itself. To compare the different places of the puddles, the other puddle water (points 2–7) concentration was 2–25 ng L^{-1}, which was comparable to point 1 (the concentration was 20 ng L^{-1} at the time), and rainwater. Studies involving fragrance substances in rainfall are very limited, and only a few reports were found. Peters *et al.*[44] measured xeno-estrogenic compound concentrations for the rainfall water nationwide in the Netherlands, and the target compounds included DPMI, HHCB, AHTN, and MK. The most frequently detected compound was HHCB (50/50 samples), followed by AHTN, (44/50 samples) and the level was 2.3–25 ng L^{-1}, which was comparable to our results.

Other than those for domestic sewage, different patterns can be seen for DOC, FCs, and PAHs. DOC followed the order: puddle ∼ USD A > rain. The five FCs followed the order: USD > rain ∼ puddle, and the pattern for the three PAHs was rain ∼ puddle ∼ USD A.

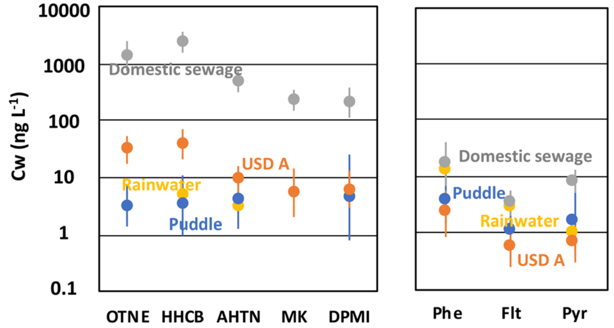
The observed pattern differences potentially reflect the source, air/water/solid partition, and/or biological/photolytic/hydrolysis decomposition differences. Because the targeted compounds are not regarded as very reactive substances and the transfer from rain precipitation to discharge *via* puddles occurs in a shorter time compared with regional or global transference, decomposition difference is not expected to play a primary role. For the air/water/solid partition, in terms of the octanol–water partition coefficient (K_{ow}) and Henry's constant, log K_{ow} is in the order of four to seven, whereas Henry's constant is from 0.001 to 1000 Pa m^3 mol^{-1} (Fig. S3†). Prior to the discussion of the transfer, the water transfer direction is naturally presumed to be from rain to puddle and puddle to USD A, but it is not necessarily limited only to this passage. However, this path cannot occur in reverse, at least for the primal path. In the passage from rain or puddle to USD A, the concentrations of the five FCs increased; in contrast, those of the three PAHs decreased. However, this difference cannot be simply explained by the phase change. For the liquid–solid change, the decrease in concentrations observed for the three PAHs from absorption in the path should have occurred similarly or to a greater extent for the five FCs because K_{ow} is similar to or higher for the latter. Meanwhile, the liquid–air change cannot be explained by the vaporization difference alone. This is because the vaporization difference would have resulted in the concentration decreasing more for the five FCs because their Henry's constant is far greater than that of the three PAHs.

Unlike the partition or decomposition processes, leakage from domestic sewage can compellingly explain such concentration changes. If the increased concentrations of the five FCs at USD A were attributable to domestic sewage, this increase would have occurred similarly for the three PAHs. In this case, the increased concentrations for the three PAHs must be negligible because the concentration ratio of USD A to domestic sewage was only in the order of one-hundredth for the five FCs. In this regard, the concentrations of the three PAHs did not significantly increase, which does not contradict the stated case. The fact that the concentration decreased from puddle to USD A should be explained by some different processes. Still, as mentioned earlier, a partition change or decomposition cannot be an alternative explanation for the increased concentrations of the five FCs at USD A.

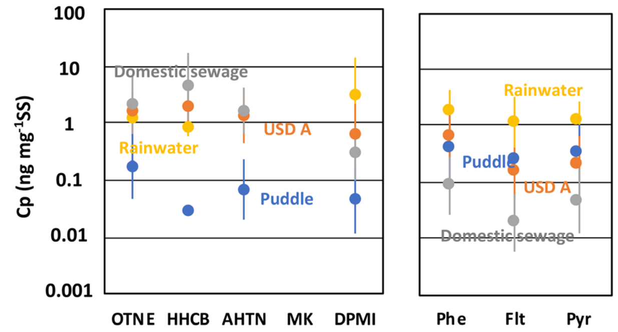
Overall, the five FCs' high concentrations may reasonably be attributed to domestic sewage. Meanwhile, the three PAHs are considered to be from atmospheric fallout,[45,46] including rainfall, as measured in our results (19 ± 8.8 ng L^{-1}; Fig. 2), or from roadside particulate matter, which is presumably mainly emitted from vehicle transportation activities in urban areas.[34,47]

To consider the effect of the solid–liquid partition in more detail, the dissolved phase concentrations, particulate phase content per SS weight, and the solid–liquid partition coefficient K_p, denoted by the following, are shown for every compound (Fig. 3).

a) Dissolved phase concentration



b) Particulate phase content



c) K_p

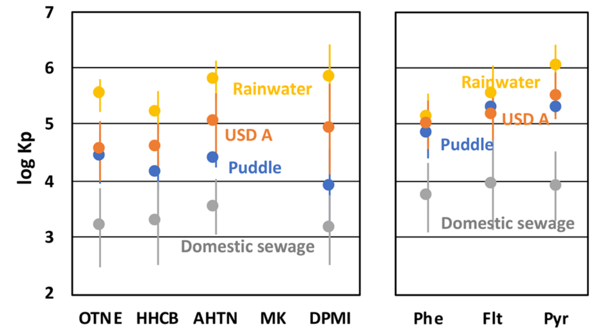


Fig. 3 Comparison of different stages for a) dissolved phase concentration, b) particulate contents, and c) K_p (geomean ± sd; musk ketone K_p was not calculated because the particulate phase content was note detect for most cases).

$$K_p\ [\mathrm{L\ kg^{-1}\ SS}] = (\text{solid contents } [\mathrm{ng\ kg^{-1}\ SS}])/(\text{liquid concentration } [\mathrm{ng\ L^{-1}}])$$

For log K_p, the ratios were fairly invariant within the five-FC group and three-PAH group, but quite different in different environmental stages. Among them, the domestic sewage ratios were commonly the lowest. This is very interesting because if the partition is normally influenced primarily by the organic matter contents in the solid phase,[48,49] then K_p would have been the highest because the organic matter contents are normally very high for domestic sewage. Unfortunately, we cannot discuss this further because the organic matter contents in SS were not measured in our study. Some different processes possibly influence this partition, and it is suggested that the partition is not in equilibrium at least in either of the environmental stages.

Concentration distribution of the storm drain pitches

From the first sampling campaign at USD A, the five FCs concentration was substantially higher at USD A than rainwater or urban surface loading. This implies that there is possibly extra input subsurface infiltration in the storm drain networks. In order to determine if there are some specific infiltration points having a spike-high concentration of the five FCs in the network, storm drainage standing waters were collected from the storm drain pitches during no-rainfall periods in the area. In some cases, the water was almost standing. However, the waters generally moved a little and seemed to comprise the base flow during the no-rainfall time. The field concentration patterns are shown in Fig. 4 and 5 as averages. These are not the results of systematical areal and spatial measurements, and are not necessarily enough approximations of the true spatial distribution of this area. For example, the low concentration points (points K, C, M, E, P, and I) would not mean they are never contaminated by these substances. Further routine measurements are required for this proof. Still, the consistency of these measurements of "clean" level implies the background level of this area. Conversely, the points marked with high values (points N, J, and Q) would be suspected to be the points of contamination. The SS concentration was clearly divided into two categories: higher (25–98 mg L^{-1}) and lower (1–9 mg L^{-1}). The DOC also followed a similar trend with some exceptions. The five FCs' concentrations drastically differed by points (18–1399 ng L^{-1}, CV = 158%), with a significantly higher variation than that of the three PAHs (23–247 ng L^{-1}, CV = 96%). This difference was also found for the dissolved phase (CV = 144% and 93% for the five FCs and 16 PAHs, respectively). A similar trend was also found for the particulate phase (CV = 191% and 93% for the five FCs and 16 PAHs, respectively), but the difference was suppressed when evaluating on the basis of the SS contents (ng g^{-1} SS; CV = 71% and 54% for the five FCs and 16 PAHs, respectively). This implies that the variation was mainly driven by the dissolved phase and was most notable for FCs.

For the FCs, we found three stable high-concentration points (Q, N, and J) where the concentrations for the five FCs were 897–1399 ng L^{-1}, comparable with those for the five FCs in domestic sewage (5273–7288 ng L^{-1}). For point Q, the water was taken from a branch pipe outlet, rather than a major open channel (Fig. S2†). At one time in a field observation, the water discharged occasionally and intermittingly despite no rainfall, suggesting that there are some discharges other than standing rain residues, and the high concentrations of the five FCs may be attributed to this undefined source. For point J, the drain was directly connected only to the upstream point N. This indicated that the water at point J directly comes from point N, and that these two points must practically be just one hot spot.

Besides the samplings, the electrical conductivity (EC) was measured on a day with no rainfall, and their patterns were then compared (Fig. 4c). The EC values were higher for the higher FC concentration points, but were not necessarily simply correlated with them. Fig. 6 shows the relation between EC and the sum of the five FCs for the dissolved phase of the drainage samplings. The FCs' concentrations tended to increase with EC, but not necessarily. If the place-

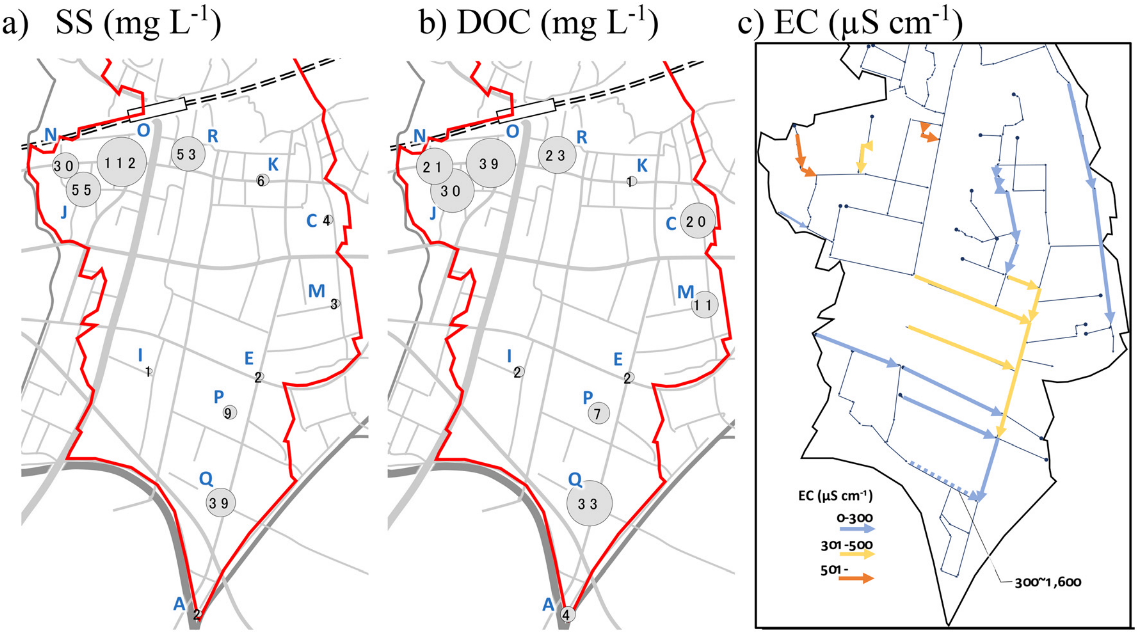


Fig. 4 Spatial distribution of conventional water indices (EC field measurements were conducted in '21/08/05; lines in the area indicate the main storm drainage network; filled circles indicate the upper most point for the drainage).

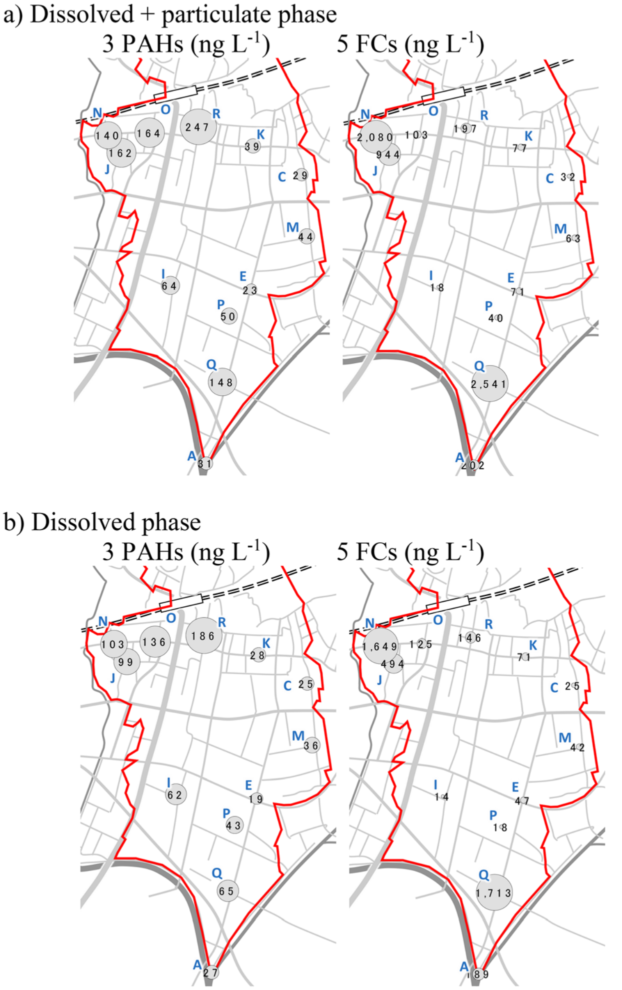


Fig. 5 Spatial distribution of 3 PAHs and 5 FCs concentration for a) dissolved + particulate phase and b) dissolved phase concentration.

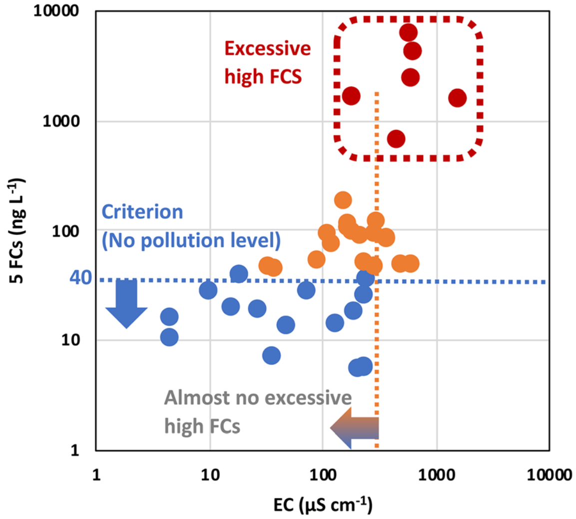


Fig. 6 EC and 5 FCs concentration of dissolved phase.

specific pollution criterion of the FCs was set to around 40 ng L^{-1}, which mostly exceeded the rainfall concentration level (mean + sd was 34 [= 22 ± 12] mg L^{-1} or the highest value of 44 ng L^{-1} for rainwater), the points having <100 μS cm^{-1} of EC would mostly meet the criterion. Furthermore, there were at least no excessively high concentrations (>200 ng L^{-1}) would be found for the points below this criterion. In addition, excessively high concentrations were mostly found for >300 μS cm^{-1}. Because of the simplicity of the handling and measurements of the EC meter, the EC values are good indicators for in-field screening.

Collectively, we found two high-concentration points for domestic-use chemicals (*i.e.*, the five FCs): points Q and N. Possible sources include the accidental spills of personal-use perfumes, cleaning, and others from some openings of storm pipes, such as gratings or leakages from domestic sewer pipelines, or misconnections. For both Q and N, the concentrations were measured several times for different rainfall intervals to ensure that the high concentrations were not accidental, and the concentrations were almost always higher than 200 ng L^{-1} (198–2541 ng L^{-1} for point Q [n = 7] and 549–2208 ng L^{-1} for N [n = 7]). For point Q, we found from a document of the city bureau that one household, located very close to being upstream of the point, was unconnected to the domestic sewer pipeline. Some graywater may be discharged from the household. However, the precise situation was not determined because of privacy concerns. Still, although further exploration was not possible due to legal barriers, the authors showed the effectiveness of the use of targeted compounds as tracers of inflows of domestic sewage.

Meanwhile, for points N and J, no possible household inflow was suggested primarily in the vicinity and along the upstream storm pipelines both by the information from the city bureau and the field survey around the area, including some interviews of the residents. Thus, further field observation was conducted occasionally to justify the high concentrations of the FCs. During such field observation, a discharge from one small hole was found accidentally on a wall in a subsurface stormwater channel connecting to point J (Fig. S4†). Water was found flowing for a time, and high concentrations of fragrances were detected in the water (790 and 1350 ng L^{-1} [n = 2]). This hole was connected to an old pipeline (seemingly a domestic sewer pipeline) because two small manholes for this pipeline were found, and the term "sewage" was engraved on the manhole surface. However, this old pipeline was not the sewer pipeline because the true sewer pipeline runs just next to it, which was validated by the official sewer map published by the municipality. Moreover, no other pipeline was registered there. Upon further exploration, we found that this line seemed to start just around 30 m away from the other end. The role of this old pipe was not clarified even upon inquiry to a section of the sewer pipeline management office in the city bureau afterward. Nonetheless, this pipeline seemed to be a vestige of an old sewer pipeline (probably from 50 years back). We found no households disconnecting to the sewer pipelines (unlike the household near point J mentioned above) around this vestige, at least nominally. If the intermittent discharge with a very high concentration of FCs was some discharge of domestic wastewater, this must have been due to some unintentional misconnection. Actually, point N was in the historical district, or old town, and on the former historical principal road. The town area is dated back to several hundred years. There may be historically some community sewage drainage systems. When the pipeline was replaced by the municipalities, some old misconnection was possibly left behind. The construction date of the municipality was also older, dating back to the 1980s (see Fig. 1, "Domestic sewer piepline"), and the detailed record was possibly lost. With this respect, points R and K are also in the same old town area, having similarly older sewer pipelines. However, the road pavement was renewed about ten years ago, and the storm drains were also most likely renewed at that time. The sewer leakages must be blocked by the renewal, if existing, and this may have resulted in our stable lower fragrance concentrations.

For further examination, some different methodologies would be required, such as the on-site investigation of possible misconnecting households. Still, the candidates for some leakages were focused down to very limited ranges, indicating the effectiveness of this methodology.

Lastly, the usage and the limitation of this methodology are discussed. The points are as follows: first, we applied fragrance substances as a tracer of domestic sewers; second, PAHs were applied for reference; third, the rain and urban surface puddle water concentration were measured and compared with those of domestic sewer and urban drainage. There are many trace organic substances that are introduced for tracers of domestic sewers, such as artificial sweeteners, drugs, caffeine, and others. Among them, fragrance substances were shown to be a promising application for the monitoring of sewer leakage, although the application of such fragrance substances is rather limited to date.[11,20,50] At the same time, a limitation was also unveiled by the results, *i.e.*, the background effect of rainwater. The fragrance substances were contained in rain and puddle water in the 1–10 ng L^{-1} range. The level was 0.1–1% of those of domestic sewage. This may be due to volatilization from domestic usage, and the effect should be clarified in the future. Considering the influences of the leakages of direct domestic sewages into storm discharges, this indicates that an infiltration-loading contribution cannot be proved by these substances if the contribution is just an order of one percent. Although this finding showed the drawbacks of the application of the substances, the significance of the measurements of rainwater and subsequent ground surface water was shown by this study. The measurements of such compounds in rainwater were very limited.[44] Our study showed that there should be further investigations in the future.

Conclusions

In this study, the concentrations of domestic-use chemicals were measured for the discharges and residues of sewer pipelines during no-rainfall times in an old urban drainage area with a separated sewer system. The concentrations were generally not high, and were comparable with those of surface puddles and rainwater itself. However, in some cases, the detected concentrations were very high and comparable with those of domestic wastewater. These high concentrations were observed stably in some limited, specific points. This suggests some leakages of domestic wastewater that are not time-accidental, but point-specific. The authors found two high-concentration points. One point was presumed to be from a household discharge unconnected to the sewers, and the other was suggested to be the leakage from a vestige of an old sewer pipeline, which is unintentionally connected with some domestic sewer.

These days, the deterioration of infrastructures is becoming a concern for developed countries, including Japan. Among these, domestic sewer pipeline deterioration is one important issue. Pipeline renewal and earthquake resistance are pressing issues for the sustainability of urban areas. However, pipeline renewal is not progressing well because of the financial limitations of governments. With this predicament, effective prioritization is important, which requires an important technique for deterioration diagnosis. However, this is not easy, especially as sewer pipelines are hidden in subsurface areas and given the extreme total length of these pipes. Thus, there must be not just one ultimate technique for such diagnosis, and our methodology is just one of such techniques.

One diagnosis difficulty is that measurements of chemicals are not so simple for wide aerial surveillance. Still, in some cases, measurements are easier than direct eye or camera observations of sewer pipelines, especially in congested urban areas. Another possible merit of such measurements is that they can detect resultant thin leakages directly even in cases when the crack is difficult to observe directly by eye or using cameras. Presently, extraction and measurement methods such as GC/MS are unfortunately not easy as routine tasks. However, as our study suggested, this method can be more effective if it is combined with simple EC measurements as screening methods. Furthermore, if the required detection level is proven at a certain level, for example, at around one to several hundreds of ng L^{-1} in our case, the minimum requirement of the sampling volume can be lessened to just a hundred milliliters or less per sample, making the whole pretreatment processing far easier. Moreover, mass spectrometry with chromatographic instruments could become a more affordable commodity technique in the future.

The extent and spread of influence can be discussed if the long-time average loading is evaluated from a set of consecutive measurements. In this study, we did not conduct flow rate measurements combined with concentration measurements; instead, the measurements were performed just intermittently. Thus, we fell short of knowing the leakage loading qualitatively. For the next step, the evaluation of mass loading and the extent of leakage in areal scales would be possible through consecutive measurements at the final discharge point (at USD A in our case). The significance of the methodology of this investigation is that we introduced a process for indicating the point of leakage with limited effort. The choice or combination of this kind of probing technique and systemic loading quantification on aerial scales would become important according to the demands of future surveying. In the future, a comprehensive approach to detecting and evaluating loading, and its combination with eye/camera observations shall become necessary techniques for old sewer pipeline management.

Conflicts of interest

There are no conflicts to declare.

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References

1 U. S. Environmental Protection Agency (EPA), *National Conference on Sanitary Sewer Overflow (SSOs)*, Seminar Publication, 1996, p. EPA/625/R-96/007.

2 L. Wolf, C. Zwiener and M. Zemann, Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks, *Sci. Total Environ.*, 2012, **430**, 8–19, DOI: **10.1016/j.scitotenv.2012.04.059**.

3 N. Ozaki, T. Yamauchi, T. Kindaichi and A. Ohashi, Stormwater inflow loading of polycyclic aromatic hydrocarbons into urban domestic wastewater treatment plant for separate sewer system, *Water Sci. Technol.*, 2013, **79**, 1426–1436, DOI: **10.2166/wst.2019.143**.

4 O. Panasiuk, A. Hedström, J. Marsalek, R. M. Ashley and M. Viklander, Contamination of stormwater by wastewater: a review of detection methods, *J. Environ. Manage.*, 2015, **152**, 241–250, DOI: **10.1016/j.jenvman.2015.01.050**.

5 D. DeSilva, S. Burn, G. Tjandraatmadja, M. Moglia, P. Davis, L. Wolf, I. Held, J. Vollertsen, W. Williams and L. Hafskjold, Sustainable management of leakage from wastewater pipelines, *Water Sci. Technol.*, 2005, **52**, 189–198.

6 M. Rutsch, J. Rieckermann, J. Cullmann, J. B. Ellis, J. Vollertsen and P. Krebs, Towards a better understanding of sewer exfiltration, *Water Res.*, 2008, **42**, 2385–2394, DOI: **10.1016/j.watres.2008.01.019**.

7 J. B. Ellis, D. M. Revitt, J. Vollertsen and D. J. Blackwood, Sewer exfiltration and the colmation layer, *Water Sci. Technol.*, 2009, **59**, 2273–2280, DOI: **10.2166/wst.2009.271**.

8 L. Wolf, *Influence of leaky sewer systems on groundwater resources beneath the City of Rastatt. Germany — Abschätzung der Grundwasserbeeinflussung durch defekte Abwasserkanäle im Gebiet der Stadt Rastatt, Karlsruhe: Schriftenreihe Angewandte Geologie*, Universität Karlsruhe, 2006, vol. 75.

9 J. B. Ellis, D. M. Revitt and L. Lundy, *Behaviour of selected emerging pollutants in stormwater best management practices (BMPs), 8th International Conference on Sustainable Technologies and Strategies in Urban Water Management (NovaTech)*, 23–27 Jun 2013.

10 S. Spahr, M. Teixido, D. L. Sedlak and R. G. Luthy, Hydrophilic trace organic contaminants in urban stormwater: occurrence, toxicological relevance, and the need to enhance green stormwater infrastructure, *Environ. Sci.: Water Res. Technol.*, 2020, **6**, 15–44, DOI: **10.1039/C9EW00674E**.

11 I. I. Buerge, T. Poiger, M. D. Müller and H. R. Buser, Caffeine, an anthropogenic marker for wastewater comtamination of surface waters, *Environ. Sci. Technol.*, 2003, **37**, 691–700, DOI: **10.1021/es020125z**.

12 N. Sankararamakrishnan and Q. Guo, Chemical tracers as indicator of human fecal coliforms at storm water outfalls, *Environ. Int.*, 2005, **31**, 1133–1140, DOI: **10.1016/j.envint.2005.04.002**.

13 S. Sauvé, K. Aboulfadl, S. Dorner, P. Payment, G. Deschamps and M. Prévost, Fecal coliforms, caffeine and carbamazepine in stormwater collection systems in a large urban area, *Chemosphere*, 2012, **86**, 118–123, DOI: **10.1016/j.chemosphere.2011.09.033**.

14 H. Yin, M. Xie, L. Zhang, J. Huang, Z. Xu, H. Li, R. Jiang, R. Wang and X. Zeng, Identification of sewage markers to indicate sources of contamination: Low cost options for misconnected non-stormwater source tracking in stormwater systems, *Sci. Total Environ.*, 2019, **648**, 125–134, DOI: **10.1016/j.scitotenv.2018.07.448**.

15 B. Sercu, L. C. Van De Werfhorst, J. L. Murray and P. A. Holden, Sewage exfiltration as a source of storm drain contamination during dry weather in urban watersheds, *Environ. Sci. Technol.*, 2011, **45**, 7151–7157, DOI: **10.1021/es200981k**.

16 S. Zgheib, R. Moilleron and G. Chebbo, Priority pollutants in urban stormwater: part 1 - case of separate storm sewers, *Water Res.*, 2012, **46**, 6683–6692, DOI: **10.1016/j.watres.2011.12.012**.

17 Y. O. O. Hu, N. Ndegwa, J. Alneberg, S. Johansson, J. B. Logue, M. Huss, M. Käller, J. Lundeberg, J. Fagerberg and A. F. Andersson, Stationary and portable sequencing-based approaches for tracing wastewater contamination in urban stormwater systems, *Sci. Rep.*, 2018, **8**, 11907, DOI: **10.1038/s41598-018-29920-7**.

18 S. Lee, M. Suits, D. Wituszynski, R. Winston, J. Martin and J. Lee, Residential urban stormwater runoff: A comprehensive profile of microbiome and antibiotic resistance, *Sci. Total Environ.*, 2020, **723**, 138033, DOI: **10.1016/j.scitotenv.2020.138033**.

19 E. Ishii, Y. Watanabe, T. Agusa, T. Hosono and H. Nakata, Acesulfame as a suitable sewer tracer on groundwater pollution: A case study before and after the 2016 Mw 7.0 Kumamoto earthquakes, *Sci. Total Environ.*, 2021, **754**, 142409, DOI: **10.1016/j.scitotenv.2020.142409**.

20 K. Osenbrück, H. R. Gläser, K. Knöller, S. M. Weise, M. Möder, R. Wennrich, M. Schirmer, F. Reinstorf, W. Busch

and G. Strauch, Sources and transport of selected organic micropollutants in urban groundwater underlying the city of Halle (Saale), Germany, *Water Res.*, 2007, **41**, 3259–3270, DOI: **10.1016/j.watres.2007.05.014**.

21 A. Müller, H. Österlund, J. Marsalek and M. Viklander, The pollution conveyed by urban runoff: A review of sources, *Sci. Total Environ.*, 2020, **709**, 136125, DOI: **10.1016/j.scitotenv.2019.136125**.

22 U. Klaschka, P. C. von der Ohe, A. Bschorer, S. Krezmer, M. Sengl and M. Letzel, Occurrences and potential risks of 16 fragrances in five German sewage treatment plants and their receiving waters, *Environ. Sci. Pollut. Res.*, 2013, **20**, 2456–2471, DOI: **10.1007/s11356-012-1120-9**.

23 M. Clara, O. Gans, G. Windhofer, U. Krenn, W. Hartl, K. Braun, S. Scharf and C. Scheffknecht, Occurrence of polycyclic musks in wastewater and receiving water bodies and fate during wastewater treatment, *Chemosphere*, 2011, **82**, 1116–1123, DOI: **10.1016/j.chemosphere.2010.11.041**.

24 M. Carballa, F. Omil and J. M. Lema, Comparison of predicted and measured concentrations of selected pharmaceuticals, fragrances and hormones in Spanish sewage, *Chemosphere*, 2008, **72**, 1118–1123, DOI: **10.1016/j.chemosphere.2008.04.034**.

25 K. Bester, J. Klasmeier and T. Kupper, Emissions of OTNE (Iso-E-super) - mass flows in sewage treatment plants, *Chemosphere*, 2008, **71**, 2003–2010, DOI: **10.1016/j.chemosphere.2008.02.004**.

26 K. Bester, Retention characteristics and balance assessment for two polycyclic musk fragrances (HHCB and AHTN) in a typical German sewage treatment plant, *Chemosphere*, 2004, **57**, 863–870, DOI: **10.1016/j.chemosphere.2004.08.032**.

27 J. D. Berset, T. Kupper, R. Etter and J. Tarradellas, Considerations about the enantioselective transformation of polycyclic musks in wastewater, treated wastewater and sewage sludge and analysis of their fate in a sequencing batch reactor plant, *Chemosphere*, 2004, **57**, 987–996, DOI: **10.1016/j.chemosphere.2004.07.020**.

28 M. Carballa, F. Omil, J. M. Lema, M. Llompart, C. García-Jares, I. Rodríguez, M. Gómez and T. Ternes, Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant, *Water Res.*, 2004, **38**, 2918–2926, DOI: **10.1016/j.watres.2004.03.029**.

29 R. Kanda, P. Griffin, H. A. James and J. Fothergill, Pharmaceutical and personal care products in sewage treatment works, *J. Environ. Monit.*, 2003, **5**, 823–830, DOI: **10.1039/b306355k**.

30 N. K. Stamatis and I. K. Konstantinou, Occurrence and removal of emerging pharmaceutical, personal care compounds and caffeine tracer in municipal sewage treatment plant in Western Greece, *J. Environ. Sci. Health, Part B*, 2013, **48**, 800–813, DOI: **10.1080/03601234.2013.781359**.

31 Y. Lv, T. Yuan, J. Hu and W. Wang, Seasonal occurrence and behavior of synthetic musks (SMs) during wastewater treatment process in Shanghai, China, *Sci. Total Environ.*, 2010, **408**, 4170–4176, DOI: **10.1016/j.scitotenv.2010.05.003**.

32 N. Nakada, M. Yasojima, Y. Okayasu, K. Komori and Y. Suzuki, Mass balance analysis of triclosan, diethyltoluamide, crotamiton and carbamazepine in sewage treatment plants, *Water Sci. Technol.*, 2010, **61**, 1739–1747, DOI: **10.2166/wst.2010.100**.

33 N. Ozaki, M. Nosaka, H. Uemura, T. Kindaichi and A. Ohashi, Degradation and volatilization process of fragrance materials and triclosan in wastewater treatment plant – Comparison between field survey and laboratory experiment, *Environ. Technol. Innovation*, 2019, **16**, 100438, DOI: **10.1016/j.eti.2019.100438**.

34 N. Ozaki, Y. Takamura, K. Kojima and T. Kindaichi, Loading and removal of PAHs in a wastewater treatment plant in a separated sewer system, *Water Res.*, 2015, **80**, 337–345, DOI: **10.1016/j.watres.2015.05.002**.

35 C. Berardi, D. Fibbi, E. Coppini, L. Renai, C. Caprini, C. Scordo, L. Checchini, S. Orlandini, M. C. Bruzzoniti and M. Del Bubba, Removal efficiency and mass balance of polycyclic aromatic hydrocarbons, phthalates, ethoxylated alkylphenols and alkylphenols in a mixed textile-domestic wastewater treatment plant, *Sci. Total Environ.*, 2019, **674**, 36–48, DOI: **10.1016/j.scitotenv.2019.04.096**.

36 M. Blanchard, M. J. Teil, D. Ollivon, L. Legenti and M. Chevreuil, Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France), *Environ. Res.*, 2004, **95**, 184–197, DOI: **10.1016/j.envres.2003.07.003**.

37 F. Busetti, A. Heitz, M. Cuomo, S. Badoer and P. Traverso, Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant, *J. Chromatogr. A*, 2006, **1102**, 104–115, DOI: **10.1016/j.chroma.2005.10.013**.

38 J. J. Liu, X. C. Wang and B. Fan, Characteristics of PAHs adsorption on inorganic particles and activated sludge in domestic wastewater treatment, *Bioresour. Technol.*, 2011, **102**, 5305–5311, DOI: **10.1016/j.biortech.2010.12.063**.

39 J. Zhao, W. Tian, S. Liu, Z. Wang, Z. Du and W. Xie, Existence, removal and transformation of parent and nitrated polycyclic aromatic hydrocarbons in two biological wastewater treatment processes, *Chemosphere*, 2019, **224**, 527–537, DOI: **10.1016/j.chemosphere.2019.02.164**.

40 Z. Liu, Q. Li, Q. Wu, D. Kuo, S. Chen, X. Hu, M. Deng, H. Zhang and M. Luo, Removal Efficiency and Risk Assessment of Polycyclic Aromatic Hydrocarbons in a Typical Municipal Wastewater Treatment Facility in Guangzhou, China, *Int. J. Environ. Res. Public Health*, 2017, **14**, 861, DOI: **10.3390/ijerph14080861**.

41 S. Sun, L. Jia, B. Li, A. Yuan, L. Kong, H. Qi, W. Ma, A. Zhang and Y. Wu, The occurrence and fate of PAHs over multiple years in a wastewater treatment plant of Harbin, Northeast China, *Sci. Total Environ.*, 2018, **624**, 491–498, DOI: **10.1016/j.scitotenv.2017.12.029**.

42 B. Nas, M. E. Argun, T. Dolu, H. Ateş, E. Yel, S. Koyuncu, S. Dinç and M. Kara, Occurrence, loadings and removal of EU-priority polycyclic aromatic hydrocarbons (PAHs) in wastewater and sludge by advanced biological treatment,

stabilization pond and constructed wetland, *J. Environ. Manage.*, 2020, **268**, 110580, DOI: **10.1016/j.jenvman.2020.110580**.

43 V. Homem, J. A. Silva, N. Ratola, L. Santos and A. Alves, Long lasting perfume–a review of synthetic musks in WWTPs, *J. Environ. Manage.*, 2015, **149**, 168–192, DOI: **10.1016/j.jenvman.2014.10.008**.

44 R. J. Peters, H. Beeltje and R. J. van Delft, Xeno-estrogenic compounds in precipitation, *J. Environ. Monit.*, 2008, **10**, 760–769, DOI: **10.1039/b805983g**.

45 D. Ollivon, H. Blanchoud, A. Motelay-Massei and B. Garban, Atmospheric deposition of PAHs to an urban site, Paris, France, *Atmos. Environ.*, 2008, **36**, 2891–2900, DOI: **10.1016/S1352-2310(02)00089-4**.

46 J. Gasperi, C. Sebastian, V. Ruban, M. Delamain, S. Percot, L. Wiest, C. Mirande, E. Caupos, D. Demare, M. D. Kessoo, M. Saad, J. J. Schwartz, P. Dubois, C. Fratta, H. Wolff, R. Moilleron, G. Chebbo, C. Cren, M. Millet, S. Barraud and M. C. Gromaire, Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric contributions for a wide range of contaminants in three French catchments, *Environ. Sci. Pollut. Res.*, 2014, **21**, 5267–5281, DOI: **10.1007/s11356-013-2396-0**.

47 S. De Pieri, A. Arruti, J. Huremovic, J. Sulejmanovic, A. Selovic, D. Đorđević, I. Fernández-Olmo and A. Gambaro, PAHs in the urban air of Sarajevo: levels, sources, day/night variation, and human inhalation risk, *Environ. Monit. Assess.*, 2014, **186**, 1409–1419, DOI: **10.1007/s10661-013-3463-1**.

48 *Partition and adsorption of organic contaminants in environmental systems*, ed. C. T. Chiou, Wiley/Interscience, New York, NY, 1st edn, 2002.

49 R. P. Schwarzenbach, P. M. Gschwend and D. M. Imdoben, *Environmental Organic Chemistry*, John Wiley & Sons, Hoboken, NJ, 2nd edn, 2003.

50 S. T. Glassmeyer, E. T. Furlong, D. W. Kolpin, J. D. Cahill, S. D. Zaugg, S. L. Werner, M. T. Meyer and D. D. Kryak, Transport of chemical and microbial compounds from known wastewater discharges: potential for use as indicators of human fecal contamination, *Environ. Sci. Technol.*, 2005, **39**, 5157–5169, DOI: **10.1021/es048120k**.