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Impacts of Emerging Contaminants on Surrounding Aquatic Environment from a Youth Festival

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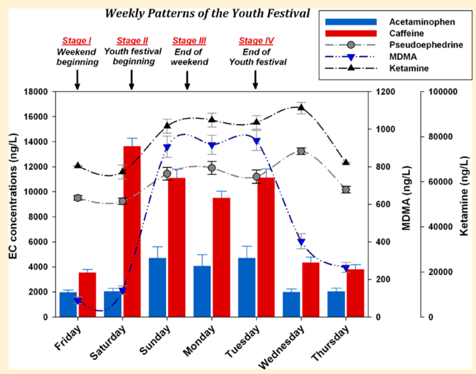
Supporting Information

ABSTRACT: The youth festival as we refer to Spring Scream, a large-scale pop music festival, is notorious for the problems of drug abuse and addiction. The origin, temporal magnitudes, potential risks and mass inputs of emerging contaminants (ECs) were investigated. Thirty targeted ECs were analyzed by solid-phase extraction and liquid chromatography coupled to tandem mass spectrometry (SPE-LC-MS/MS). Sampling strategy was designed to characterize EC behavior in different stages (before and after the youth festival), based on multivariate data analysis to explore the contributions of contaminants from normal condition to the youth festival. Wastewater influents and effluents were collected during the youth festival (approximately 600 000 pop music fans and youth participated). Surrounding river waters are also sampled to illustrate the touristic impacts during peak season and off-season. Seasonal variations were observed, with the highest concentrations in April (Spring Scream) and the lowest in October (off-season). Acetaminophen, diclofenac, codeine, ampicillin, tetracycline, erythromycin-H_2O, and gemfibrozil have significant pollution risk quotients (RQs > 1), indicating ecotoxicological concerns. Principal component analysis (PCA) and weekly patterns provide a perspective in assessing the touristic impacts and address the dramatic changes in visitor population and drug consumption. The highest mass loads discharged into the aquatic ecosystem corresponded to illicit drugs/controlled substances such as ketamine and MDMA, indicating the high consumption of ecstasy during Spring Scream.



■ INTRODUCTION

Human populations have been increasing by approximately 78 million people per year. The United Nations Population Division expects that the world's population, now estimated at 7.2 billion, could reach 8.1 billion by 2025 and up to 9.6 billion by 2050.[1] In conjunction with an increasing human population, the contaminations of aquatic environments due to human activities will also likely increase.[2,3] Emerging contaminants (ECs) are a large group of compounds such as pharmaceuticals and personal care products (PPCPs), and illicit drugs/controlled substances. EC levels in freshwater ecosystems are expected to increase with human populations and activities. Several studies in Europe and the U.S. highlight the multitude of EC levels that are present in waste, surface, drinking, and ground waters.[4,5] The widespread occurrence of these contaminants in freshwater is potentially a major problem with consequences that are yet to be fully understood.[6] Although some of the compounds have been proposed to be included in regulatory lists,[7] there is relatively little information on their ecotoxicological effects, and until now, they have escaped regulation.[8] The known environmental effects of some of the ECs include the reduction of macroinvertebrate diversity in rivers and behavioral changes in mosquito fish.[9,10]

Conventional wastewater treatment plants (WWTPs) were not designed to remove ECs.[10] The expansion and optimization of wastewater treatment processes may be the most efficient strategy to mitigate the potential effects of these contaminants. To aid this effort, one design factor that must be studied in greater detail is the temporal variability of ECs' occurrence in wastewaters. Diurnal variations in wastewater flows are common phenomena related to peak water use periods.[11] Few studies have examined temporal fluctuations in EC levels. A recent study documented the fluctuations in the loadings of prescription and illicit drugs/controlled substances in wastewater flows during the National Football League's Super Bowl weekend in a major metropolitan area of the USA.[12] Another study evaluated days of week, seasons, and winter holidays for

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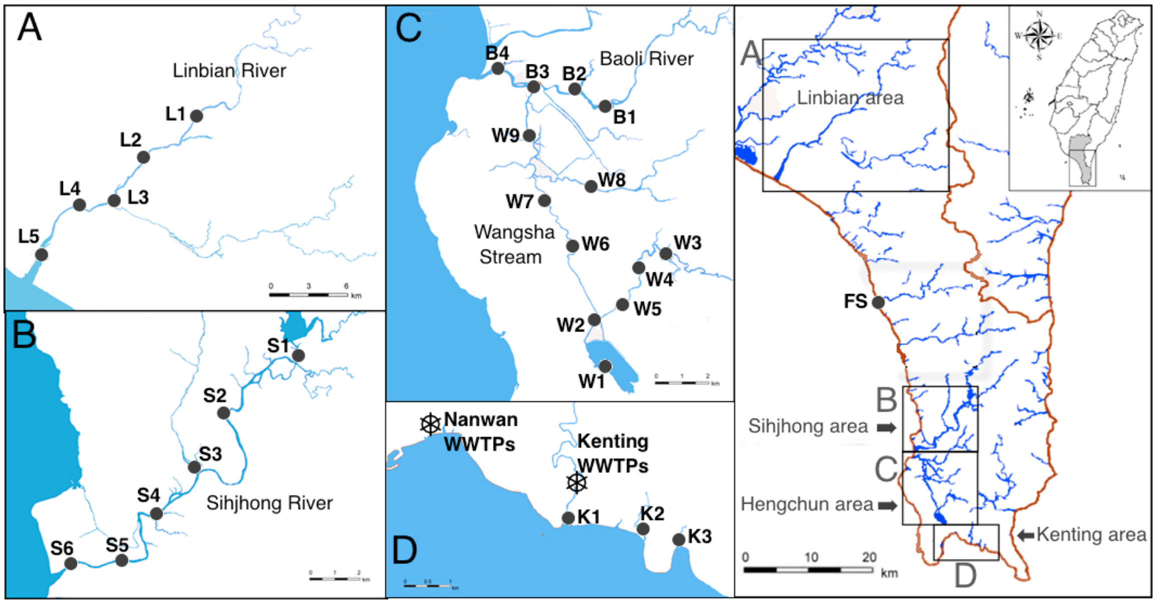

Figure 1. Map of the sampling locations (A–D) in the present study. A: sites L1–L5 are in the Linbian area; B: sites S1–S6 are in the Sihjhong area; C: sites B1–B4 and W1–W9 are in the Hengchun area; D: Nanwan WWTPs (influents and effluents), Kenting WWTPs (influents and effluents), and sites K1–K3 are in the Kenting area. (Site FS is in the estuary of Fangshan River.).

their effects on illicit drug/controlled substances concentrations in Spanish surface water.[13] The authors observed higher illicit drug/controlled substances concentrations on weekends compared to weekdays, and they also found the highest concentrations in the winter, particularly after holidays such as Christmas and New Year's Day.

Kenting and the Hengchun are located in Pingtung County in southernmost Taiwan. The beautiful landscape and ecosystem with a tropical climate attract a huge number of tourists every year, which leads to an explosion in tourism, especially during summer vacation and an annual youth festival called Spring Scream, an outdoor pop music festival held in early April in Kenting. The estimated number of tourists in the study area are 7 million persons per year.[14] As a result, a range of anthropogenic organic pollutants is discharged into the river systems and coastal environments, posing potential environmental risk to the ecosystem.[15−18] Additionally, our previous study proved that these ECs occurred widely and were transported to the coastal areas of southwestern Taiwan, and several EC compounds could pose high risks to aquatic organisms in coastal waters.[19] However, with respect to anthropogenic effects in Kenting, previous studies only focused on water quality features, such as nutrients, suspended solids, and ammonia.[20,21] To our knowledge, up to now no study has comprehensively dealt with EC residues and demonstrated the impact of tourisms and especially of a time limited mass event on the exposure of ECs to WWTPs and river waters of a whole region in the study areas. This study therefore focused on the occurrence of ECs, and characterized their behavior based on multivariate data analysis to explore the contributions of contaminants from normal condition to the youth festival as we refer to "Spring Scream". The sampling strategy was so designed to allow a thorough assessment of the potential risks, removal efficiency, and effluent inputs of a suite of ECs. The results provided important data for pollution control and management purposes for the problems of drug abuse in the youth festival.

MATERIALS AND METHODS

Materials. The chemicals and standards used (including suppliers, purities, and detailed physiochemical properties of the 30 selected ECs) are described in Text S1 and Table S1 of the Supporting Information (SI).

Study Area and Sample Collection. We investigated 30 sampling sites (28 river water samples and 2 wastewater samples) from the water systems in these sampling locations: (A) Linbian area (population density: 73.48 person/km^2): Linbian River (L1–L5); (B) Sihjhong area (population density: 53.45 person/km^2): Sihjhong River (S1–S6); (C) Hengchun area (population density: 156.03 person/km^2): Baoli River (B1–B4), and Wangsha Stream (W1–W9); (D) Kenting area (population density: 160.14 person/km^2): Nanwan WWTPs, Kenting WWTPs, and three estuary (K1–K3)(Figure 1). Linbian River has a drainage area of 336.6 km^2 and a length of 42 km. Sihjhong River has a drainage basin of 124.9 km^2, with a length of 31.9 km. One reservoir, which is the water resource and supply for agricultural and domestic usage, is located upstream of Sihjhong River. With a length of 20.7 km and a 103.2 km^2 drainage area, Baoli River with its tributary, Wangsha Stream, runs through the township of Hengchun. There are only two WWTPs (Nanwan and Kenting) exposing to the streams in the Kenting area and both of them collect the domestic wastewater from several beach resorts and hotels. In addition, almost 95% of the residential wastewaters were connected to these WWTPs. Detailed descriptions of the two WWTPs and the sampling sites are included in the SI (Table S2 and S3).

Sampling campaigns for river water and wastewater samples were implemented each time on off-season (October 2010), dry season (March 2011), youth festival (April 2011), and peak/wet season (August 2011). In addition, wastewater samples were collected everyday during the week of the youth festival (2011/4/1–2011/4/7). River water samples were obtained from a bridge or dam using a bucket. Grab samples of the influents and effluents were taken from Nanwan and Kenting WWTPs. All water samples were collected in

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precleaned amber glass bottles at each sampling site and WWTPs, and the same numbers of sites and samples were collected in each season. Following collection, the water samples were immediately sent to the laboratory, and extraction was completed within 2 weeks.

Sample Preparation and Analysis. The chemical analyses of ECs followed the methods employed in our previous study.[19] Both river water and wastewater samples were filtered through 0.7 μm glass fiber filters and then acidified to pH 6 by adding 0.1 M HCl, followed by the addition of 0.2 g/L Na_2EDTA as the chelating agent. For the solid-phase extraction (SPE) of water samples, 300 mL water samples were spiked with isotopically labeled surrogates (acetaminophen-d_4, amphetamine-d_{11}, methamphetamine-d_{14}, MDMA-d_5, $^{13}C_6$-ibuprofen, and $^{13}C_3$-caffeine) in quantifying procedural recovery. The Oasis HLB cartridge (500 mg, 6 mL, Waters, Milford, MA) was conditioned with 6 mL methanol and 6 mL deionized water. The water sample was then passed through the preconditioned SPE-cartridge at a flow rate of approximately 20 mL/min. Then, the cartridge was rinsed with 6 mL deionized (DI) water and dried for 30 min using the vacuum of the SPE manifold. The analyte was then eluted by 6 mL of methanol. The extract was evaporated to dryness under a gentle nitrogen stream. Afterward, the residue was redissolved in a final 1 mL volume with a 50:50 (v/v) solution of methanol in DI water and filtered through a 0.22 μm filter. The filtered solution was transferred into an amber autosampler vial for chemical analysis.

Concentrations of ECs were analyzed using liquid chromatography electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS). Two different methods were applied for the separation of analytes (method 1 for PPCPs and method 2 for illicit drugs/controlled substances), and both were performed using an Agilent 1200 series chromatograph (Agilent, Palo Alto, CA) interfaced with an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) operated in positive and negative modes. The injection volumes for method 1 and method 2 were 50 and 10 μL, respectively, and the autosampler was operated at 25 °C. The gradients and mass spectrometer conditions used are described in the Text S1 and Table S4−S5 of the SI.

Method Performance. SI Table S6 presents recoveries for the target analytes in DI water, river water, and effluents. For all the compounds, wide linearity ranges were obtained for the quantification. Seven to 10 points' calibration curves were constructed using least-squares linear regression analysis, and subjecting them to the same SPE procedures used for the environmental water samples spiked with the analytes, typically from 0.5 to 2000 ng/L with $r^2 > 0.9991$ for all compounds. Recovery experiments were performed on DI water, river water, and effluent samples spiked with 500 ng/L target analytes and isotopically labeled surrogates to estimate the precision, recovery, and accuracy of the analytical method. The mean recoveries in DI water ranged from 79% to 108%, compared with 83% to 115% in river water and 69% to 128% in effluents. The mean recoveries of isotopically labeled surrogate standards were 82 ± 13% (acetaminophen-d_4), 87 ± 11% (amphetamine-d_{11}), 85 ± 12% (methamphetamine-d_{14}), 78 ± 9% (MDMA-d_5), 92 ± 8% ($^{13}C_6$-ibuprofen), and 89 ± 11% ($^{13}C_3$-caffeine), respectively. Field and procedural blanks were treated as controls for possible contamination in the laboratory and in field sampling. Analysis of these blanks demonstrated that the extraction and sampling procedures were free of contamination. The limits of detection (LOD) were defined as signal-to-noise (S/N) ratios of 3, and the limits of quantification (LOQ) were defined as signal-to-noise (S/N) ratios of 10. The results indicated that the LOQ for each compound ranged from 0.04 ng/L to 3 ng/L for DI water, from 0.04 ng/L to 10 ng/L for river water, and from 1 ng/L to 10 ng/L for effluent samples (SI Table S6). Overall, the validation data, such as repeatability, recoveries, and LOQ were good, so the reliable determination of these target compounds was feasible.

Mass Loads Estimation. Although runoff and discharge of untreated waters cannot be neglected but since precise data is not available, this contribution was not taken into consideration. To calculate the EC mass loads to the aquatic environments, the concentrations detected in two WWTPs effluents (SI Table S9) were considered as well as the flow rate of effluent discharges (SI Table S3). The input to the aquatic environments were calculated according to the following:

$$\text{mass loads(g/d)} = [\text{concentration of pollutants(g/m}^3)] \times [\text{flux of water(m}^3\text{/d)}]$$

Multivariate Statistical Analysis. Principal component analysis (PCA) was performed on the data set using the SPSS 16.0. PCA is a multivariate technique which looks for a reduced set of new orthogonal variables or principal components, which explain maximum data variance and allow for an easier data interpretation of the correlations existing among the original variables and samples.[22] PCA is applied to the matrix of experimental data whose rows are the samples and whose columns are the variables or analyzed ECs. The data sets from all water types were used including river waters, WWTP influents and effluents. The set of samples was subdivided in four different groups according to sampling date: dry season, youth festival, peak/wet season, and off-season. Each principal component (PC) is interpreted by means of the loadings (linear combination of the original variables) which describe the composition of the possible contamination sources and by the coefficients or scores, whose numerical values give information about the contribution of these sources (described by the principal components) to the samples. Principal components are ordered sequentially according to the amount of explained data variance. The concentrations were Kaiser normalized and Varimax rotation was used as the preferred transformation.

RESULTS AND DISCUSSION

Temporal and Spatial Variation. The detailed concentration levels for river waters and wastewaters, the average removal efficiency for 26 ECs in the WWTPs, and the numbers of visitors in the Kenting area can be found in the SI (see Table S7−S9, Text S3, and Figure S4−S5). During the four sampling seasons, 5 of the 30 target ECs (fluoxetine, benzophenone-3, heroin, cocaine, and cannabinol) were not detected at any river water sample. Only cannabinol could not be found in any wastewater sample. Both omeprazole and heroin are usually highly metabolized and hydrolyzed, suggesting their metabolites (such as 5-hydroxyomeprazole, morphine, and 6-acetylmorphine) should be further monitored. Generally, among the 25 detected ECs in river water, ampicillin showed the highest detection rate (79%), followed by codeine, caffeine, carbamazepine, and pseudoephedrine at 63%, 62%, 61%, and 57%, respectively. Aside from these five predominant compounds, all other ECs were found at lower detection

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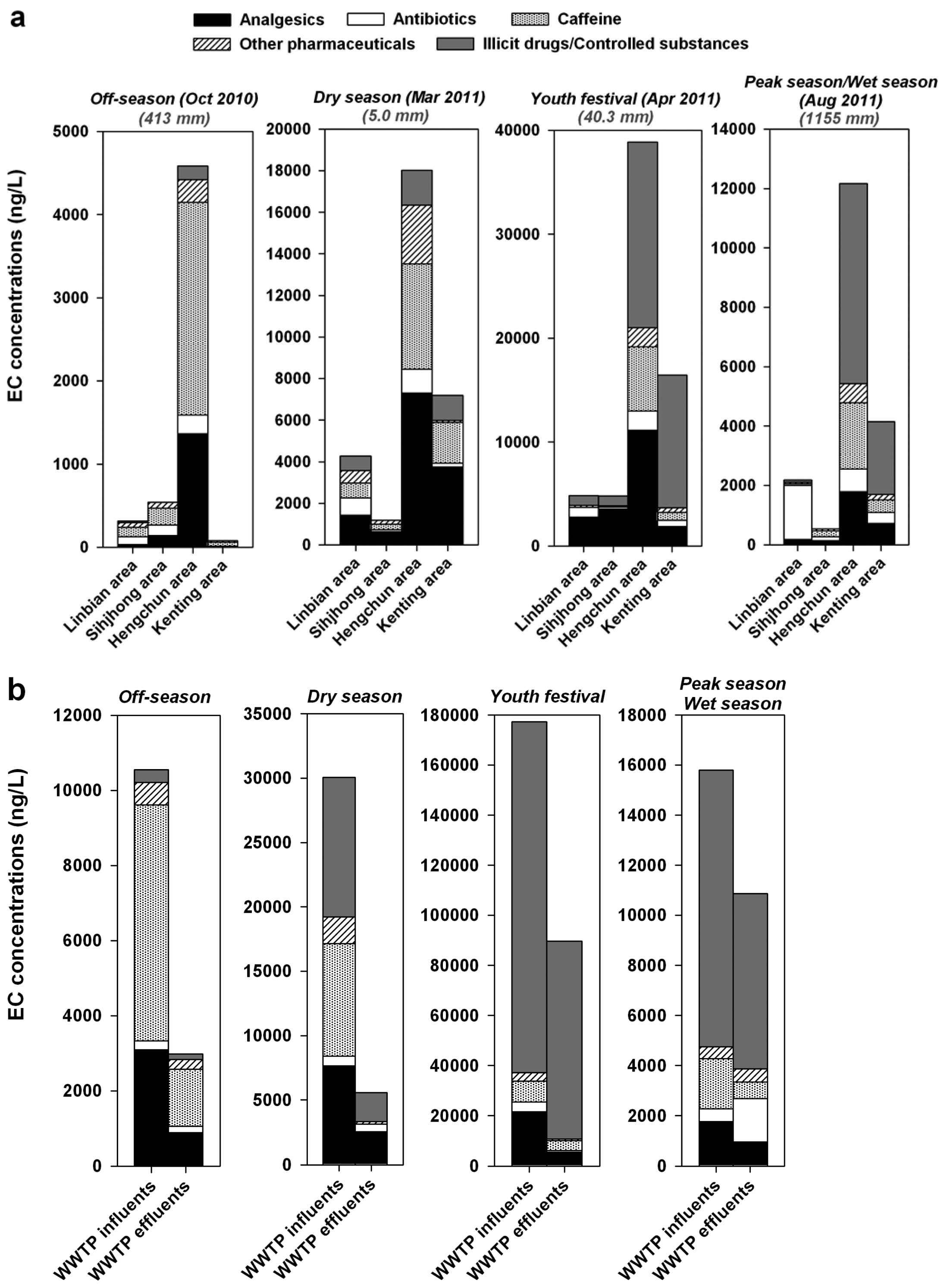

Figure 2. (a) Temporal and spatial variation of ECs in river water samples in the study area. The values at the bracket show the mean monthly rainfall amounts (mm). (b) Temporal and spatial variation of total ECs in wastewater samples of two WWTPs in the Kenting area.

rates (<44%), especially omeprazole, which was detected sporadically at a rate of 12%. On the other hand, most ECs were frequently present in wastewater; 20 of the 30 EC compounds were detected in more than 90% of the samples. Concentrations across all the detected ECs in river water and wastewater ranged from ND (not detected) to 9533 ng/L (ketamine) and from ND to 138 000 ng/L (ketamine), respectively. Ten substances had peak concentrations >1000 ng/L, including ketamine (138 000 ng/L), pseudoephedrine (44 667 ng/L), caffeine (13 633 ng/L), acetaminophen (8433 ng/L), codeine (3967 ng/L), gemfibrozil (2400 ng/L), ibuprofen (1500 ng/L), erythromycin-H_2O (1463 ng/L), sulfamethoxazole (1280 ng/L), and MDMA (1267 ng/L). Several analgesics (acetaminophen, ibuprofen, and codeine) observed at high concentrations could be attributed to the fact that these compounds are commonly used as antiphlogistic drugs, with widespread use in the treatment of cold symptoms, aches, pains, and arthritic conditions.[3,23] Concentrations of

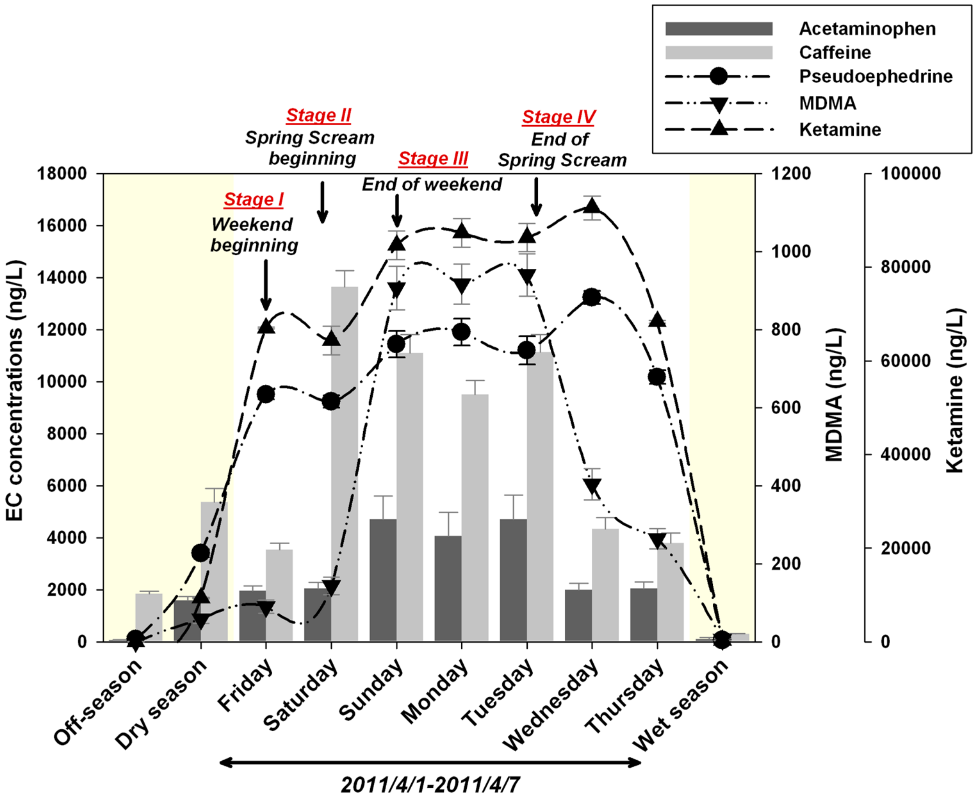

Figure 3. Weekly patterns of caffeine, acetaminophen, pseudoephedrine, ketamine and MDMA during Spring Scream in the Kenting WWTP influents (replicated samples: n = 3).

caffeine were also found at high levels, which is not entirely surprising given its prevalence in beverages, foods, and pharmaceuticals.[24,25]

The overall concentrations of ECs were highest in April (during the youth festival) compared to other seasons, while most of the lowest concentrations were detected in October (off-season) and August (wet season). As shown in Figure 2, both river water and wastewater had the highest EC levels in April, followed by March, August, and October. This can clearly be attributed to greater dilution during the wet season by heavy rainfall and enormous numbers of tourists during the special event. The amount of rainfall in March and April was only about 5.0−40 mm, while the rainfall amount reached 413 mm in October and 1154.7 mm in August. It is consistent with previous studies that weather conditions such as precipitation and sunlight are the main factors affecting the concentration levels of ECs.[26] In addition, the biodegradation and photodegradation of ECs might be stronger in the summer than in the winter due to higher microbial activity and strong sunlight in summer.[27] In general, the concentrations of target analytes were found to be considerably high during dry weather conditions, including the youth festival period, and significantly reduced during wet weather due to the significant dilution of from precipitation.

EC levels in the Hengchun area were generally higher than those in Sihjhong area and Linbian area (Figure 2a). Although Hengchun is a town with a population of 30 837 inhabitants, it is also a known holiday destination. Thus, its population could increase drastically during the holiday. Wastewaters from two WWTPs in Kenting area contained much higher concentrations of ECs than those in river waters (Figure 2b). This was probably due to the fact that (1) domestic wastewater courses draining into the sewage conduits run through all the resort and hotel areas, which could contribute a marked effect; (2) dilution in the river waters for these ECs. Furthermore, as mentioned above, Kenting hosts the largest youth festival (Spring Scream, which takes place in several venues distributed all within the Kenting area), visited by approximately 600 000 pop music fans and youth.[14] Therefore, the tremendous number of tourists in the Kenting area could serve as the main sources of ECs in the surrounding aquatic environments.

Another significant feature of the detailed spatial distributions was that the compositional profiles of ECs showed the distinct variations in regional distribution patterns (SI Figure S2). Among six categories of ECs, illicit drugs/controlled substances was the most predominant group in the Kenting and Hengchun areas (81−85%) and decreased gradually to the north, while analgesics contributed 83−95% of the total EC concentrations in the Linbian and Fangshan Rivers and showed a southward decrease. In general, these distribution characteristics imply that the levels of illicit drugs/controlled substances were affected by the influx of tourists, reflecting the important effects of holidays and the youth festival in this study.

A global comparison of detected EC concentrations in river waters and wastewaters is shown in SI Table S10. It should be noted that grab sampling was employed in this study though suffering from the known limitations. Further improvements are required in future study to obtain a representative and appropriate sampling via employment of the composite samplers.[28,29] In general, with the exception of illicit drugs/controlled substances, the concentrations of ECs in this study were lower than those reported in northern Taiwan, and in the U.S., but slightly higher or comparable to those in Japan, Korea, China, UK, and Spain. Benzophenone-3 and benzophenone-4

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levels measured in the present study were both lower than those reported in Europe.[26,30−34]

The individual RQ values of the investigated ECs were calculated to evaluate the ecotoxicological risk (see SI Figure S1 and Text S2). Seven target ECs, acetaminophen, diclofenac, codeine, ampicillin, tetracycline, erythromycin-H_2O, and gemfibrozil, could pose high risks (RQ > 1) to aquatic organisms in the Kenting area. For methamphetamine, MDMA, and ibuprofen, however, the RQ values were greater than 0.1, corresponding to moderate effects, while ketoprofen, sulfamethoxazole, clofibric acid, carbamazepine, and benzophenone-4 posed low environmental risks to the aquatic ecosystem. Although such risk assessment is a useful exercise, the results should be treated with caution, as single-compound exposure scenarios are impractical in the real environment due to the unknown effects of multiple contaminants in combination, which in itself may be of considerable ecological concern.

Behavior and Contribution from the Youth Festival. *Weekly Patterns.* In this work, wastewater samples from Kenting were collected during one whole week (2011/4/1−2011/4/7) of April 2011, which included the influents the day immediately before and after the youth festival. Concentrations of compounds that are prescribed or administered by medical personnel were generally not affected by the youth festival. For example, several pharmaceuticals such as diclofenac, ibuprofen, erythromycin-H_2O, clofibric acid, atenolol, carbamazepine, fluoxetine, and omeprazole appear to be relatively consistent in terms of magnitude and variability. Of the 10 detected illicit drugs/controlled substances, there was no distinct difference in the levels of amphetamine, methamphetamine, and FM2 for holidays and weekdays. Only trace amounts of GHB were found sporadically throughout the week. Amphetamine and methamphetamine are street drugs, and therefore no specific difference is expected. In addition, since cocaine and heroin are usually highly metabolized, suggesting further monitoring on their metabolities should be determined.

However, results of weekly profiles for five EC concentrations (caffeine, acetaminophen, pseudoephedrine, ketamine, and MDMA) in WWTPs during the special event impressively demonstrate the higher amounts of these ECs found in different stages of the week (Figure 3). In this study, four stages were identified from the characteristics of target ECs and are used for illustrations purposes hereafter. Stage I (weekend beginning) was sampled before the youth festival, so it seems to show the levels under normal conditions. A significant increase in concentration of caffeine (3733 to 13 633 ng/L) was observed from stage I to stage II (Spring Scream beginning), which could represent the outset of effects from holidays and the youth festival. The concentrations of acetaminophen, pseudoephedrine, ketamine, and MDMA showed no discernible difference during stage I and stage II, whereas their concentrations were at relatively high levels in stage III (end of the weekend), indicating an increase in the consumption of these ECs during the youth festival.

All the selected ECs maintained a rather constant abundance during stage III. After stage IV (end of Spring Scream), the EC concentrations showed a conspicuous decline, reflecting the levels of off-season, dry season, and wet season as normal conditions. With respect to the tourist impacts, the most interesting finding was the extraordinary increase (89.1 to 940 ng/L) in the party drug MDMA (ecstasy) during the youth festival. This drug was only detected at a very low level before and after the youth festival. Therefore, the noteworthy presence of this compound might be due to MDMA abuse that coincided with the Spring Scream.

As outlined above, data obtained on ECs in influents during the youth festival in the present study are dramatic and interesting. The prominent increases in the occurrence of ECs were in agreement with data reported regarding similar events. Lai et al.[35] reported that high levels of MDMA and cocaine use were observed on New Year's Eve. Similarly, higher MDMA concentrations could be linked to graduation festivities[36] and a big dance party.[37] Thomas et al.[38] also observed that the highest concentrations of illicit drugs/controlled substances were commonly found on weekends, as well as increased cocaine consumption on weekends compared to weekdays.

Principal Component Analysis. The observed concentration profiles shown in Figure 3 demonstrate a general trend of several EC levels and the effects of holidays and the youth festival in influents from WWTPs in the Kenting area. Principal component analysis (PCA) further demonstrates the impacts of the youth festival and tourists. Among the 30 ECs analyzed, 23 detected compounds were considered for PCA. Values such as "below the detection limit" were set to half the value of LOQ. The contribution of each variable to every principal component (PC) is shown in SI Table S11. The explained variance by component is also included. The first three PCs, which explain 66.1% of the variance contained in the original data set, had an eigenvalue of greater than one. The first principal component (PC1) accounted for 30.9%, whereas the second and third components accounted for 23.4% and 11.8%, respectively. Loading scores higher than 0.32 were considered meaningful.[39]

The first component (PC1) had high positive loadings for most of the dominant ECs (acetaminophen, ibuprofen, codeine, sulfamethoxazole, caffeine, gemfibrozil, atenolol, amphetamine, methamphetamine, ketamine, pseudoephedrine, and MDMA), indicating a similar origin for these compounds. The positive loadings of these compounds correlated with their high abundance in the Kenting area and suggested that the discharge of these ECs from WWTPs affects this component (PC1). The second component (PC2) had positive loadings for diclofenac, ketoprofen, naproxen, ampicillin, carbamazepine, benzophenone-4, and FM2, while the third component (PC3) described a contamination pattern with relatively high loadings for tetracycline. Altogether, these PCs could describe the temporal variability, with positive contributions for compounds with the highest abundance in the March (dry season) and April (Spring Scream) campaigns.

Figure 4 illustrates the score plots for PC1 vs. PC2, and two groups could be distinguished. The most noticeable group included samples from the Kenting area. These samples had higher positive score values for both PC1 and PC2, which indicated the touristic impacts and was affected by the youth festival. In contrast, the relevant group included samples with low score values for both PC1 and PC2. Samples with a low abundance of ECs (negative score values for PC1 and PC2) comprised most October (off-season) campaigns, indicating a nontouristic impact. Overall, once a data set was obtained by successive reconnaissance campaigns, PCA could be a useful tool to assess the origin and spatiotemporal contamination patterns. Therefore, PC1 vs. PC2 score plots evidenced the effects of holidays and the youth festival, and touristic and nontouristic impacts.

Mass Loads. Weekly and seasonal mass loads (g/d) of five EC groups (analgesics, antibiotics, caffeine, other pharmaceuticals, and illicit drugs/controlled substances) from effluents are

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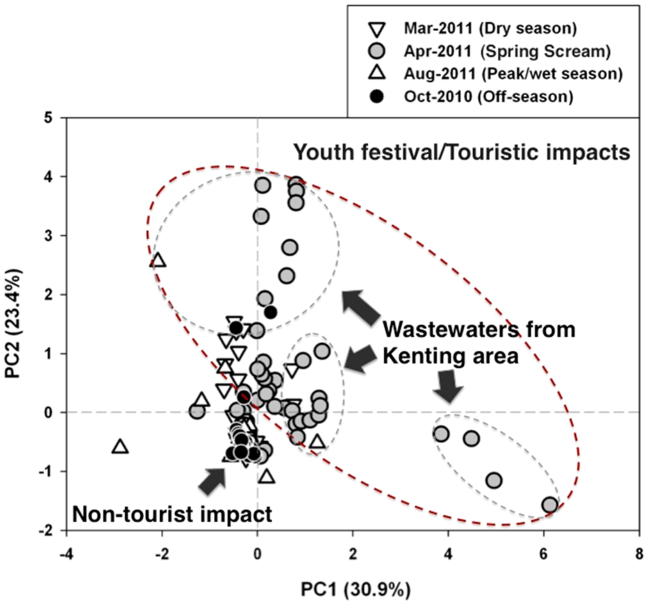

Figure 4. PCA scores of the different sampling campaigns in all river waters and wastewaters: PC1 vs PC2.

shown in SI Figure S3. A notable increase in weekly mass loads was observed during the tourist-affected period due to the much higher inputs of illicit drugs/controlled substances in wastewater (SI Figure S3a). This might be expected, as there was a strong increase in the number of tourists and amount of consumption during the youth festival. The highest weekly mass loads discharged toward the aquatic ecosystem corresponded to illicit drugs/controlled substances such as ketamine and MDMA, indicating the high consumption of ecstasy during Spring Scream. In addition, the mass loads of ECs exhibited strong seasonal variability in the study area (SI Figure S3b). Approximately 90% of the total EC inputs occurred during the youth festival and peak season, clearly because the number of tourists was remarkably higher during these periods. In contrast, only 3.8% of the total EC inputs were contributed during the off-season. The total annual inputs of ECs amounted to 13 950 g per year in the study area. Of this total, illicit drugs/controlled substances contributed the highest proportion of inputs (64.5%), followed by analgesics (20.8%), caffeine (6.3%), antibiotics (5.7%), and other pharmaceuticals (2.7%). Although precise data for the event attendees during the youth festival was not available, we could still estimate the EC contribution per person of whole youth festival (2011/4/1−2011/4/7) based on the mass inputs and approximately numbers of total attendees. It was suggested that a total 0.56 mg EC contribution per person was estimated for the youth festival. The annual inputs of the individual ECs ranged from 29.9 to 5710 g per year. Among these ECs, pseudoephedrine, ketamine, acetaminophen, caffeine, and codeine were the five predominant ECs, with annual inputs of 5710, 3123, 1619, 877, and 824 g per year, respectively. These total EC inputs from the WWTP effluents would be discharged into the aquatic ecosystem.

Environmental Implications. Strong evidence on the enhanced flow of a specific spectrum of illicit drug/controlled substances (ketamine, MDMA) in different stages of the week suggests that the youth festival played an important role in characterizing the changes of visitor population and drug consumption. At the same time, it was reported that the annual quantity of drugs seized in Taiwan reached 3500 kg in 2011 and that ketamine (2594 kg) accounted for 74% of the total drugs seized.[40] Together with our findings, they implied that the problems of drug abuse and addiction during the youth festival, and consequent environmental issue are of concern.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on the river systems, treatment plants, detected compounds, analytical methods, quality assurance, and detailed figures and tables on concentrations, removal rates, and risk assessments. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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