High Anthropogenic Organic Matter Inputs during a Festival Increase River Heterotrophy and Refractory Carbon Load

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ABSTRACT: Streams and rivers metabolize dissolved organic matter (DOM). Although most DOM compounds originate from natural sources, recreational use of rivers increasingly introduces chemically distinct anthropogenic DOM. So far, the ecological impact of this DOM source is not well understood. Here, we show that a large music festival held adjacent to the Traisen River in Austria increased the river’s dissolved organic carbon (DOC) concentration from 1.6 to 2.1 mg L$^{-1}$ and stream ecosystem respiration from −3.2 to −4.5 mg L$^{-1}$. The DOC increase was not detected by sensors continuously logging absorbance spectra, thereby challenging their applicability for monitoring. However, the fluorescence intensity doubled during the festival. Using parallel factor analysis, we were able to assign the increase in fluorescence intensity to the chemically stable UV-B filter phenylbenzimidazole sulfonic acid, indicating organic compounds in sunscreen and other personal care products as sources of elevated DOC. This observation was confirmed by liquid chromatography coupled with mass spectrometry. The elevated respiration is probably fueled by anthropogenic DOM contained in beer and/or urine. We conclude that intense recreational use of running waters transiently increases the anthropogenic DOM load into stream ecosystems and alters the fluvial metabolism. We further propose that chemically distinct, manmade DOM extends the natural range of DOM decomposition rates in fluvial ecosystems.

1. INTRODUCTION

Streams and rivers transport dissolved organic matter (DOM) from the terrestrial ecosystem to the oceans.1,2 Along this journey, most fractions of DOM are metabolized, resulting in an overall predominance of heterotrophy in fluvial ecosystems.3,4 Most DOM compounds transported in streams originate from natural sources such as soil organic matter.1,5 Since the advent of organic synthesis, however, scientists have created an unprecedented diversity of organic compounds for human use.6 We define anthropogenic DOM as any organic compound dissolved in water originating from organic synthesis, biotechnological production, or human excretion. Yet, with a few exceptions,7 fluxes of chemically diverse anthropogenic DOM into fluvial ecosystems have received little attention.8

In Europe, impacts from outdoor sports, leisure, and recreational activities have been ranked as among the top 10 threats to freshwater ecosystems.9 The global predicted rise in tourism by 2050 is estimated to result in a 90% increase in water resource use as compared to 2010.10 Extreme cases of recreational activities impacting rivers are festivals (Figure 1). Thousands of visitors may camp along the shores and spend a significant time in the water. Studies of swimming pools suggest that humans can introduce substantial amounts of anthropogenic DOM from sweat, personal care products, hair, and skin as well as urine and feces.11,12 Previous studies on large festivals have already shown significant alterations of adjacent aquatic ecosystems, caused by the introduction of pharmaceuticals and drugs into river water.13,14 However, so far, no previous study has addressed the effects of a large cultural event on DOM fluxes and stream metabolism.

We assessed the impact of the FM4 Frequency music festival with approximately 50,000 visitors per day over the festival’s 4 day duration held in the immediate vicinity of the Traisen River in Austria. First, we investigated if inputs of anthropogenic DOM during the festival can be detected by high-frequency absorbance sensors15 and fluorescence spectroscopy. Fluorescence data were analyzed by parallel factor analysis (PARAFAC),16 a powerful tool to identify dominant fluorescence components in bulk DOM samples.17 Second, we explored if anthropogenic DOM sources alter river ecosystem metabolism as estimated from continuous dissolved oxygen measurements.18 Ecosystem metabolism, summarized as net
ecosystem production (NEP), is the balance between gross primary production and ecosystem respiration and defines a river’s role as a carbon sink or source. As heterotrophs metabolize DOM, the metabolic balance of a river directly depends on the DOM availability.\textsuperscript{19−21} Stream metabolic rates have also been shown to respond to land-use change,\textsuperscript{22−24} urbanization,\textsuperscript{25,26} and wastewater effluents.\textsuperscript{27,28} Accordingly, shifts in metabolic rates can be considered as a powerful indicator of human repercussions. We hypothesized that a strong presence of humans in a river enhances DOM inputs and extends the natural range of DOM decomposition rates. Finally, we predict that deliveries of potentially labile anthropogenic DOM stimulate ecosystem respiration and enhance heterotrophy.

2. METHODS

2.1. Study Area and Experimental Setup. The Traisen River is a tributary of the Danube River in Austria with a mean annual discharge of 14 m$^3$s$^{-1}$ at the city of St. Pölten.\textsuperscript{29} The catchment consists of agricultural, forested, and urban areas. The headwaters are located in the mostly forested pre-alpine region of Lower Austria. The river has been subject to intense measures of river regulation. For example, artificial ground sills frame the river bed. Also, the bed was straightened with embankments to avoid flooding.\textsuperscript{30} The Traisen River is subject to various uses. Upstream of the sampling sites, approximately 10 m$^3$s$^{-1}$ of the river discharge, is diverted into two industrial side channels.\textsuperscript{31} Thus, some sections of the festival reach can become fragmented during elongated dry spells. A separate sewage channel transports the wastewater of the city and suburban areas to a wastewater treatment plant located 30 km downstream. The Traisen River can thus be subject to organic contamination\textsuperscript{32} during very high flows, when wastewater retention tanks overflow.

The FM4 Frequency festival is one of the largest music festivals in Europe and is held annually at the Traisen River (around 200,000 visitors from August 16 to 19 2018, 50,000 on each day). The festival offers campgrounds along the banks of the river and the organizers explicitly promote bathing opportunities.\textsuperscript{33} During the festival, the river receives considerable amounts of waste (e.g., packaging, cleaning products, food leftovers, urine, and feces). The floating fraction of this waste is largely retained by an oil barrier that is installed by the organizers as a preventive measure for the duration of the festival (Figure 1).

We positioned UV−vis probes (Spectro::lyser, S::can Messtechnik GmbH, Vienna, Austria) and HOBO dissolved oxygen loggers as well as HOBO pendant temperature/light 64K loggers (Onset Computer Corporation, Bourne, MA, USA) upstream (48°09'56"N, 15°37'44"E) and downstream (48°11'39"N, 15°38'01"E) of the festival area (reach length = 3.8 km). We measured from July 2 to October 14 at the downstream site and from late July to mid-September upstream. UV−vis absorbance spectra covering the range from 220 to 735 nm with 2.5 nm increments were logged automatically every 15 min. The dissolved oxygen and temperature/light probes were cleaned manually once per week and daily during the festival. The UV−vis probe was

![Figure 1. (A) Recreational use of the Traisen River, Austria during the FM4 Frequency music festival. (B) Oil barrier installed downstream of the festival area. Particulate matter is retained, while dissolved compounds can transfer downstream during the 4 day festival.](https://dx.doi.org/10.1021/acs.est.0c02259)
cleaned automatically with compressed air once per hour. To measure DOC from UV−vis, the manufacturer’s global calibration was applied; systemic deviations were compensated for (Supplementary Text 1).

Manual samples were drawn weekly before and after the festival and daily during the festival for DOC, DOM, and liquid chromatography−mass spectrometry (LC−MS) analysis in the laboratory. In addition, a 24 h sampling during the most active time of the festival (Saturday, August 18 at 3 pm, to Sunday, August 19, 2 pm) was performed using ISCO automated samplers (Teledyne ISCO, Lincoln, NE, USA), taking one sample per hour. The samples for DOM and DOC were filtered immediately in the field (Whatman, GF/F filters, pore size 0.7 μm) into precombusted borosilicate glass vials and stored in a cool environment during transport. Samples were stored at 4 °C in the dark and analyzed within a maximum of 4 days. Unfiltered water was frozen at −20 °C upon return to the laboratory until sending for LC−MS analysis.

2.2. Laboratory Measurements. DOC analysis was performed on a GE-Sievers 900 TOC analyzer (SUEZ Water Technologies & Solutions, Trevose, PA, USA) operating with the persulfate oxidation method and an inorganic carbon removal unit. DOM absorbance spectra at wavelengths 200 to 700 nm with 0.5 nm steps were acquired in the lab using a UV−vis spectrophotometer (Shimadzu UV 17000, Shimadzu Corp., Kyoto, Japan) in 5 cm cuvettes. Excitation emission matrices (EEMs) were measured by a Hitachi F-7000 (Hitachi Ltd. Corp., Tokyo, Japan) fluorescence spectrophotometer from 1 cm quartz cuvettes. Fluorescence intensities were measured at excitation (ex) wavelengths from 240 to 450 nm at 5 nm increments and emission (em) wavelengths from 250 to 550 nm at 2 nm increments.

Phenylbenzimidazole sulfonic acid (PBSA, C₁₃H₁₀N₂O₃S) was analyzed from frozen samples by LC−MS. After thawing, a volume of approximately 10 mL of each sample was filtered through a 0.2 μm pore size regenerated cellulose syringe filter (Sartorius, Germany) directly into an autosampler vial and weighed. Prior to analysis, 2.5 ng of isotopically labeled internal standard (IS) carbamazepine-D₁₀ (Chiron AS Stiklestad, Norway) was added to the samples. Blank samples and calibration curves were prepared using 10 mL of bottled drinking water (Dobra voda, Czech Republic) and adding 2.5 ng of IS, and for the calibration curve, the native standard (NS) ensulizole by Sigma-Aldrich (ranging from 0.05 to 50 ng) was used. The matrix matching standard was prepared by adding 2.5 ng of IS and 50 ng of NS to 10 mL of river water sample from the upstream control site.

LC−MS/MS analysis was performed with a TSQ Quantiva triple-stage quadrupole mass spectrometer, coupled with an Accela 1250 LC pump (both Thermo Fisher Scientific, USA) and an HTS XT-CTC autosampler (CTC Analytics AG, Switzerland). We used a Hypersil Gold aQ column (50 mm × 2.1 mm i.d., 5 μm particles, Thermo Fisher Scientific, USA).

From each sample, 100 μL was directly injected onto the column using the settings described by Grabic et al. When PBSA concentrations exceeded the calibration range, samples were diluted with drinking water (10× or 100×) and reanalyzed. Results were calculated using a combination of internal standards and matrix matching according to the method described by Grabic et al. and Grabicova et al.

2.3. Parallel Factor Analysis. We used the “Nway” and “drEEM” matlab toolbox to correct our raw EEMs and perform the PARAFAC analyses with different data subsets. Specifically, we analyzed one PARAFAC model (global model = g) that included all measured river EMMs, while a second model (reduced model = r) only contained river data from samples that were not affected by the festival (Supplementary Text 2 and Figure 2). Third, we computed one individual model for each anthropogenic DOM source. The similarity of the model components was then analyzed with the modified Tucker’s congruence coefficient (TCC).

Figure 2. EEM of (a) Traisen sample upstream and (b) Traisen sample downstream of the festival from August 18 (third festival day). (c) PARAFAC-modeled component with sunscreens containing PBSA dissolved in MQ. (d) Excitation (solid lines) and emission (dashed lines) spectra of Traisen festival component C₃g (red), sunscreen with PBSA (blue), and beer (yellow).
2.4. Net Ecosystem Production Calculations. We computed net ecosystem production (NEP) upstream and downstream of the festival based on continuous dissolved oxygen measurements for a duration of 2 months. For this, the Bayesian approach of the "StreamMetabolizer" R-package was applied\(^9\) (Supplementary Text 3 and Table S1 3). Air pressure data were provided by the Austrian Federal Institute of Meteorology (ZAMG) from the nearby meteorological station of St. Pölten.

2.5. Incubation Experiments. According to field observations, we considered the following sources of anthropogenic DOM in our laboratory incubations (for details, see Supplementary Text 4): beer, urine, cosmetic leachate, shampoo, toothpaste, sunscreen, and soap. After initial tests, pure PBSA (Sigma-Aldrich, Vienna, Austria) was also tested. All substances were dissolved in deionized (MQ) water and then filtered through GF/F filters. DOM absorbance and fluorescence spectra were measured following the methods outlined previously.

Respiration and DOC degradation of the three most prominent anthropogenic DOC sources—beer (Kaiser Bier, Braunion Österreich AG, Wieselburg, Austria), urine, and sunscreen—were measured in Traisen water, filtered through precombusted GF/F filters 1 day before setting up the incubations. We dissolved two types of sunscreens separately (Nivea Bronze SPF 30 and Nivea Protect & Refresh SPF 20; Beiersdorf AG, Hamburg, Germany), urine, and beer to final concentrations of 11.6, 4.1, 7.4, and 9.9 mgC L\(^{-1}\), respectively, with GF/F-filtered Traisen water. All DOC sources were also filtered through precombusted GF/F filters. The prepared media were then inoculated with 2% unfiltered river water and respiration rates measured in 100 mL Schott bottles equipped with oxygen sensor spots (SP-PS3-NAU, PreSens, Regensburg, Germany). Oxygen was measured every 2 to 12 hours, depending on the concentration decline. Each treatment was incubated with four replicates; additional replicates of each treatment were filled into 40 mL glass vials. From these vials, DOC degradation rates were obtained by measuring the decline of DOC concentration over time (at start and after 2, 7, 14, and 28 days, respectively) by laboratory analysis. In addition, the DOM fluorescence and absorbance were measured in triplicate at the beginning of the incubations as well as after 2 and 28 days. All bottles and vials were incubated in the dark at 20 °C and constantly shaken.

Respiration is given in mgC L\(^{-1}\) day\(^{-1}\) and calculated from oxygen consumption using 1 as a conversion factor.\(^{59}\) DOC decay rates (kDOC) were calculated as $DOC(t) = DOC_0 \cdot e^{-kt}$ with the initial (DOC\(_0\)) and DOC\(_n\), with \(t\) as the time in days and \(k\) as the exponential decay coefficient (day\(^{-1}\)). Subsequently, half-lives of the sources were calculated as $ln(2)/k$. Plotting the DOC degradation over time confirmed a first-order process of DOC degradation for the first week.

2.6. Statistics. Linear relationships between variables were considered significant at \(p < 0.001\). To evaluate the impact of the festival on DOC concentrations independent of upstream and downstream conditions at random. Thus, this test can address before-after-impact-control problems, even when dependence among sites, sequential observations, and heteroscedasticity may be present\(^{40}-^{42}\) (Supplementary Text 5). To account for potential autocorrelation, the RIA significance level was set to \(\alpha = 0.10\). As discharge is a major driver of DOC and NEP, we included only days with a similar discharge (+25%) to that of the festival period of 6 m\(^3\) s\(^{-1}\) into the analysis. Differences of microbial respiration and DOC half-lives between different DOC sources were analyzed with a one-way ANOVA followed by Tukey’s post-hoc analysis. Data were first checked for normal distribution and equal variances; respiration data were log-transformed to fulfill the criteria for ANOVA. All statistical tests were run in R.\(^{43}\) Tukey’s post-hoc tests were done with the glht function of the “multcomp” R-package.\(^{44}\)

### 3. RESULTS AND DISCUSSION

#### 3.1. Festival Effects on DOC Concentration and DOM Composition

During non-festival conditions, downstream UV–vis DOC concentrations showed a significant linear relationship with discharge ($r^2 = 0.56, p < 0.001, n = 9008$) and an anticlockwise hysteresis following high-flow events (Supplementary Figure 3). This indicated varying soil contributions as the main source of DOC variability,\(^{45}\) a common feature of temperate streams.\(^{46,47}\) To evaluate the role of DOC and NEP on DOC concentrations independent of discharge, we selected all periods with a discharge similar to that at the time of the festival (6 m\(^3\) s\(^{-1}\) ± 25%) into a data subset.

At the downstream station, laboratory DOC concentrations were higher during the festival (average 1.94 ± 0.31 mg L\(^{-1}\)) than at the non-festival period in both locations (average 1.53 ± 0.50 mg L\(^{-1}\), RIA D = 0.2671, \(p < 0.01, n = 34\)). Conversely, no upstream or downstream differences during the festival...
were detected by sensors in UV–vis-based DOC estimates (RIA \( p = 0.426, n = 1945 \)) or in the absorbance at 340 nm (\( A_{340} \)) measured in the laboratory (RIA \( p = 0.329, n = 30 \)). \( A_{340} \) is a common proxy of DOC and was also significantly related to laboratory DOC in the Traisen River before and after the festival (\( r^2 = 0.63, p < 0.001, n = 24 \)). During the festival, however, no significant relationship was detected (\( r^2 = 0.18, p = 0.033, n = 26 \)). This uncoupling showed that a new DOM source with low absorption properties was introduced into the stream as a result of the festival.

To investigate the chemical signature of the festival-specific DOM input, we applied two PARAFAC models on excitation–emission data. A global model (g) that encompassed all fluorescence data, including the festival samples, revealed six components (Table 1, Figure 2a, and Supplementary Text 2). A second reduced model (r), which excluded the downstream festival samples, yielded only five components (Table 1 and Figure 2b). The five components present in both models included three humic-like and two protein-like substances. These components are common in rivers and are typically referred to as C3g, C4g, and C6g. However, during the festival, a new previously undescribed PARAFAC component (C3g, excitation at 300 nm, maximum emission at 344 nm, Table 1) was detected at the downstream site (Figure 2).

Besides this new component, the maximum fluorescence intensity in Raman units of the protein-like component C4g (also named tryptophan-like peak “T”) was significantly higher than in the pre-festival period (RIA \( D = 0.014, p < 0.01, n = 31 \)). This peak is commonly attributed to bacterial activity and contamination. Its increase suggests that the festival caused either a higher microbial activity of the established microbial communities or led to bacterial contamination of the river through human excretion. The C4g component was found to exhibit similar fluorescence characteristics to various pharmaceuticals and also agreed with the fluorescence characteristics of beer, soap, and urine in our lab incubations (Table 2). The significant increase of the C4g component during the festival thus suggests that some of these substances were likely introduced during the festival and stimulated microbial activity.

Finally, the tyrosine-like peak (C6g) has previously been used as a fluorescence indicator for festival-associated pharmaceuticals such as ibuprofen and carbamazepine in wastewater. However, we observed no change of the fluorescence intensity of C6g (zero Raman units) during the festival, suggesting that these substances were not introduced in an amount detectable by fluorescence spectroscopy. Instead, we attribute any variation of this component to variations in primary production in early summer (Figure 3).

### 3.2. DOM Increase by Sunscreen

To elucidate the origin of the new festival DOM component, we analyzed the fluorescence of various potential anthropogenic DOM sources dissolved in deionized water (MQ). The sources included different sunscreens, beer, urine, and others (Table 2). When analyzing the fluorescence of sunscreen dissolved in MQ, the resulting PARAFAC component had an emission and excitation similarity score of TCC = 0.97 with the new C3g festival component of g (Figure 2d). This component absorbed light at 300 nm, where its concentration is masked by the presence of natural humic substances that also strongly absorb at this wavelength. Specifically, the excitation peak of component C3g is located between 295 and 305 nm, absorbing light at the same wavelengths as C3g.

We analyzed several sunscreens dissolved in MQ and found that only the ones containing PBSA resulted in a high fluorescence intensity per unit carbon (1.63 RU L mgC\(^{-1}\)). Finally, pure PBSA dissolved in MQ showed excitation–emission maxima at 300 and 348 nm, precisely matching the peak found in most sunscreens containing PBSA (TCC > 0.96). Moreover, pure PBSA agreed with the C3g festival component in the river (TCC = 0.99). Given this strong agreement in fluorescence properties, we conclude that organic compounds of sunscreen acted as a main source of anthropogenic DOM in the Traisen River, enhancing the festival DOC concentration.

PBSA is an organic UV-B filter commonly used in sunscreen and has been detected previously in wastewaters and freshwaters. Within the European Union, cosmetic products can contain up to 8% (m/m) PBSA, making personal care products a very likely source of PBSA in freshwaters subject to recreational use.

We used fluorescence intensity to estimate the potential contribution of sunscreen to the river DOC load (Supplementary Text 4). First, we determined the apparent fluorescence intensity in Raman units per carbon mass (RU mgC\(^{-1}\)) for different sunscreens that contained PBSA. The range was between 0.76 and 3.00 RU L mgC\(^{-1}\) (average 1.63 RU L mgC\(^{-1}\)). Second, we determined the average fluorescence intensity of the C3g festival component during the 24 h festival sampling at the downstream site (0.79 ± 0.17 RU L, peak 1.26 RU L) and corrected this value by subtracting the average fluorescence (0.04 ± 0.02 RU L) of the upstream control site. Finally, we divided the stream value by the average fluorescence intensity of all sunscreens. Accordingly, we predicted that the sunscreen contributed approximately 0.48 mgC L\(^{-1}\) to the downstream DOC concentration in the Traisen River during the most intense 24 h period of the festival.

Two more lines of evidence confirm our conclusions. First, calculations of the potential sunscreen use by festival visitors demonstrate the general feasibility that sunscreen can act as a main source of DOC during the festival. Previous works have shown that average sunscreen users apply ~1 mg cm\(^{-2}\) of skin surface area, resulting in a potential contribution of 20 g of sunscreen for each visitor and application. Assuming a 10% mass loss leached as DOC (dissolving experiments with different sunscreens after 30 min of mixing in MQ water, Supplementary Text 4 and Table S1) and 50,000 bathing festival visitors in the river per day, we expected a leached DOC mass of 100 kg. With the average water flow of 6 m\(^3\) s\(^{-1}\), this mass can increase the river DOC concentration by 0.20 mg L\(^{-1}\). Interestingly, this estimated value agrees well with the...
observed average difference in DOC concentration of 0.23 mg L\(^{-1}\) between the upstream and downstream sampling sites during the entire festival period.

Second, PBSA quantified by LC–MS confirmed a significant contribution of sunscreen and UV-filters therein to river DOC concentrations (Figure 4). While the upstream concentrations remained below 0.2 \(\mu g\) L\(^{-1}\) throughout the entire festival period, downstream concentrations increased to a maximum of 45 \(\mu g\) L\(^{-1}\) on August 18 (Figure 4). These exceptionally high concentrations exceed those previously reported for streams,\(^57\) lakes,\(^56\) and even those of open air swimming pools.\(^67\) Given that PBSA makes only a maximum of 8% of the mass of sunscreen\(^58\) or according to studies from outdoor pools,\(^67\) this measurement also suggests that roughly 0.5 mg L\(^{-1}\) DOC in the river originates from sunscreen.

We note that these observed concentration changes for PBSA and for DOC attributed to the release from personal care products are higher than any other previous studies on this topic.\(^55,57-59\) Moreover, PBSA concentrations analyzed on samples taken downstream of the festival in the days after the festival (3.6, 0.68, and 0.27 \(\mu g\) L\(^{-1}\) for 1, 2, and 4 days after the festival, respectively) indicated that PBSA persisted in the river water likely until dilution occurred. This suggests that the PBSA would also be transported downstream without major degradation, as proposed by previous works.\(^57,69\)

### 3.3. Effects of Anthropogenic DOM on Stream Metabolism

To test if festival-related anthropogenic DOM stimulates ecosystem respiration, we modeled gross primary production and ecosystem respiration from continuous oxygen measurements and calculated NEP. During the festival, NEP was significantly reduced, that is, more heterotrophic at the downstream site (\(-3.2 \pm 1.0 \text{ mgC L}^{-1} \text{ day}^{-1}\) versus \(-4.5 \pm 0.8 \text{ mgC L}^{-1} \text{ day}^{-1}\)) as compared to the days before and after the festival with similar conditions (RIA \(D = 1.33, p < 0.01, n = 24\)). Metabolic shifts toward stronger heterotrophy have been reported for rivers receiving wastewater effluents\(^28,70\) and may be caused either by a decrease in gross primary production and/or an increase in ecosystem respiration. A decrease in gross primary production may be caused, for example, by physical disturbance of benthic algae by festival visitors.\(^71\) However, no effect on gross primary production was detected (RIA \(p = 0.62\)). Instead, we found enhanced ecosystem respiration (RIA \(D = 2.60, p < 0.01, n = 24\)), likely through additions of labile anthropogenic DOM.

To explore whether anthropogenic DOM extends the natural range of DOM decomposition rates in river ecosystems, we assessed the biodegradable DOM fraction in laboratory incubations of four anthropogenic DOM sources. We incubated two types of sunscreens, one with PBSA and one without, as well as urine and beer. We found significant differences in the respiration rates of the different anthropogenic DOM sources (Figure S1; one-way ANOVA; \(F_{(2,9)} = 204, p < 0.001\); sunscreen with PBSA excluded). Respiration rates were the highest in the incubations with beer (4.04 \(\pm\) 0.58 mgC L\(^{-1}\) day\(^{-1}\)) (Figure 4a), while the respiration of urine was one order of magnitude lower (0.40 \(\pm\) 0.14 mgC L\(^{-1}\) day\(^{-1}\)). The lowest respiration rate was determined for sunscreen. The sunscreen without PBSA (product name “Nivea”, Beiersdorf AG, Hamburg, Germany) showed only minimal dissolved oxygen uptake corresponding to a respiration rate of only 0.13 \(\pm\) 0.03 mgC L\(^{-1}\) day\(^{-1}\). For the sunscreen containing PBSA (product name “Nivea Bronze”,...
Beiersdorf AG, Hamburg, Germany), no respiratory uptake of dissolved oxygen occurred. The latter results were corroborated by fluorescence measurements, showing no reduction in fluorescence following the 28 day incubations. We therefore conclude that PBSA contained in sunscreen was not subject to any detectable microbial degradation (Figure 5a,b), suggesting that it might persist for longer time scales than those measured in our incubations in fluvial networks. Previous work has shown that PBSA was only photodegraded when H2O2 was present but otherwise remained photostable under UV radiation.69 We found however no literature on its microbial degradation.

We estimated the half-lives of the four anthropogenic DOM sources during biodegradation. They differed significantly (one-way ANOVA; \( F_{(3,8)} = 23.09, p < 0.001 \)). Beer had the shortest half-life (4.2 ± 0.2 day) followed by urine (11.4 ± 0.3 day) and sunscreen without PBSA (13.5 ± 0.3 day). Sunscreen with PBSA had a half-life of 39.1 ± 5.3 day. However, as the fluorescence intensity of PBSA remained unchanged throughout the incubation, we assume that only some compounds of the sunscreen degraded, while PBSA was refractory. This likely results in an underestimation of the half-life of sunscreen containing PBSA, when an exponential decay model is assumed. Combining the results of the incubation experiments with the observed increase in heterotrophic respiration, we assume that in addition to refractory DOM originating from personal care products, also highly labile DOM from beer, urine, and degradable sunscreen entered the stream during the festival.

3.4. Perspectives in Water Quality Monitoring. We identified the manmade organic compound PBSA as a major contributor to the fluorescence DOM pool during a large music festival. Here, PBSA served as a surrogate for organic UV filters found in personal care products. To our knowledge, this is the first study that successfully applied fluorescence spectroscopy to identify a specific compound without prior knowledge of the compound identity and its source. Our results confirm that PARAFAC is a remarkably sensitive method to detect DOM sources not previously present in a system, even if they are masked inside a complex matrix.73 In turn, our findings also demonstrate new challenges for monitoring DOM in aquatic environments. Fluorescence indices might lead to wrong conclusions as they were not developed nor tested to capture contributions of synthetic DOM (Supplementary Text 6). For example, our data would yield a higher biological index, suggesting the presence of fresh autochthonous DOM during the festival, rather than synthetic compounds, such as PBSA. Furthermore, due to its distinct optical properties, synthetic DOM might escape the traditional bulk supervision methods by optical sensors based on absorbance and single-wavelength fluorescence detection. This is also relevant for risk assessments and monitoring programs as optical sensors have become the preferred choice for quantifying DOC in these applications.15 Overall, we suggest that, with global population growth and the enhanced recreational use of rivers,71 the role of anthropogenic DOM is becoming increasingly important. Specifically, we predict that future water quality in populated regions will be deteriorated by the introduction of anthropogenic DOM with its specific properties. Festivals are a perfect opportunity to evaluate potential inputs from anthropogenic sources by recreational activities. Several studies have shown that pharmaceutics and drugs can be introduced in concentrations exceeding ecological risk levels during these events.13,53,75 Moreover, they might not be captured by water quality monitoring programs mainly targeting wastewater effluents.14 The observed change in ecosystem respiration underlines the relevance of these enhanced inputs; they demonstrate that anthropogenic DOM can have significant repercussions for the functioning of aquatic systems. Finally, we propose that the introduction of manmade organic compounds, such as PBSA, will likely extend the chemical diversity and decomposition rates of DOM in natural systems. In contrast, other manmade DOM such as beer can fuel rapid
microbial respiration, exceeding the respiration rate of natural soil leachate.76 We therefore propose that increased loads of anthropogenic DOM to rivers will ultimately alter the overall range of organic carbon decomposition rates in fluvial ecosystems.

**ASSOCIATED CONTENT**

Whereas the Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c02259.

UV–vis sensor measurements and validation, PARAFAC model validation, net ecosystem, production calculations, sunscreen fluorescence, randomized intervention analysis, and fluorescence and absorbance indices (PDF).

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Author Contributions

J.S. and M.S. conceived the study; A.H., V.A., and N.K. designed and performed the field sampling and analysis; K.A., A.H., and G.S. planned and realized lab incubations; H.S. performed the PBSA analysis; A.H., K.A., J.S., and M.S. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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