ACS ES&T Water

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Filtering Smoke, Polluting Water: Cellulose Acetate Cigarette Filters as a Rapid Source of Tobacco-Derived Chemicals

Sarah Poletti, Margaret Stack, Eunha Hoh, George Youssef, Thomas E. Novotny, and Natalie Mladenov*

Cite This: https://doi.org/10.1021/acsestwater.6c00482

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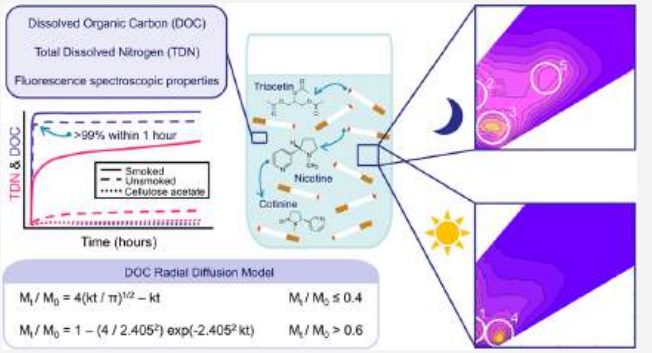
ABSTRACT: Cigarette butts, including their cellulose acetate (CA) cigarette filters (CFs), are a source of toxic chemical pollution to aquatic environments. We investigated the sources, kinetics, and environmental fate of chemicals leaching from CFs in water. Most compounds leached from unsmoked and machine-smoked CFs within 1 h, plateauing at 38.4 ± 4.8 and 41.5 ± 4.9 mg dissolved organic carbon (DOC) per gram CF, respectively. We found that CA polymer contributes negligibly to organic CF leachates. Smoked filters consistently released higher concentrations of DOC, total dissolved nitrogen (TDN), and aromatic and fluorescent compounds than unsmoked filters. We conclude that leachate fluorescence and TDN likely originate from tobacco residue, while DOC derives from both smoking and filter additives. Simulated sunlight had no effect on DOC release but the increase in TDN and reduction of nicotine-like fluorescence in smoked CF leachates reflect the transformation of aromatic alkaloids into new compounds. DOC leaching kinetics were estimated using a radial diffusion model, which confirmed that >98% of DOC was released within the first hour in ultrapure water (>85% in synthetic stormwater), and indicate surface area and internal diffusion limitations. These results inform future predictions of CF pollutant release and mitigation efforts to reduce its source.



KEYWORDS: *cigarette butts, microplastic pollution, leaching kinetics, diffusion model, fluorescence, EEM*

1. INTRODUCTION

Cigarette butts (CBs) are among the most prevalent trash items polluting coasts, with over 1.2 million CBs collected from shorelines globally in 2024 alone.[1] Cigarette butts consist of wrapping papers, plastic additives, residual tobacco, and cigarette filters (CFs), which are composed of plasticized cellulose acetate (CA) arranged in a dense microfiber matrix. During smoking, combustion byproducts adhere to the CF microfibers.[2] These fibers are shed from the filter and can be inhaled and ingested by smokers.[3] CF fibers also contribute significantly to microplastic pollution, with CFs releasing an estimated 0.3 million tons of microfibers into aquatic environments each year.[4]

Plasticizers, commonly used in CFs to promote structural stability and flexibility, contribute to plastic toxicity in aquatic environments.[5] Triacetin is the most frequently used plasticizer in cellulose acetate cigarette filters[6] and has previously been detected in cigarette butt leachates.[7] The manufacturer of Marlboro cigarettes, the brand used in this study, reports using triacetin in its filter construction.[8]

CBs may release these plasticizers when in contact with water, along with a variety of other harmful chemicals that threaten the health of marine organisms, including polycyclic aromatic hydrocarbons (PAHs),[9] heavy metals,[10] nicotine, and cotinine.[11] Organic compounds are responsible for most of cigarette butt leachate's toxicity.[12] Nicotine and cotinine, both tobacco alkaloids, are two of the most prevalent CB-derived organic compounds.[7] Nicotine is a highly water-soluble alkaloid that accounts for over 90% of total alkaloids found in tobacco.[13]

Nicotine specifically leaches from the tobacco portion of cigarettes, so it is not detected in the leachates of unused cigarette filters. Following smoking, however, nicotine becomes evenly distributed throughout the smoked filter.[14] Cotinine is a more persistent degradation product of nicotine[15] that can be formed via biodegradation, reactive intermediary oxidation, and photolysis in aquatic environments.[14,16] A major gap exists in our understanding of how these and other organic compounds derived from CFs contribute to the dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations of CB leachates, as most previous studies have

Received: April 2, 2026
Revised: June 20, 2026
Accepted: June 23, 2026

Figure 1. Materials used in leaching experiments: (a) cellulose acetate powder, (b) unsmoked cigarette filters, (c) smoked cigarette filters, and an (d) unraveled (smoked) cigarette filter.

included the tobacco portion of the cigarette butt in leachate generation.

The degradation of CBs and their components is influenced by environmental factors such as photoirradiation, which can enhance the leaching of DOC and other constituents from various plastics and additives, including polystyrene, polyvinyl chloride (PVC), bisphenol A (BPA), and diethylhexyl phthalate (DEHP).[17−19] Photoirradiation also acts as a principal driver in the breakdown of aromatic carbon compounds.[20] This photodegradation can either mineralize these compounds or convert them into new byproducts that may be more toxic or persistent than the original molecules. The specific effects of photoirradiation on the leaching of compounds from cigarette filters have not been thoroughly investigated.

In addition, it is necessary to understand how different mechanisms govern the release kinetics of organic compounds from cigarette filters. Several factors can limit the mass transfer of molecules from a solid matrix into a liquid solution. In some cases, diffusion is governed by the concentration gradient between the material and the surrounding solution (concentration gradient driven). In others, it is constrained by the available surface area at the solid−liquid interface (surface area-limited), where both external and internal controls can limit mass transfer.[21] In external diffusion control, mass transfer is restricted by the movement of molecules across the plastic surface water boundary layer.[5] Internal diffusion control occurs when the diffusion rate is limited by the movement of molecules within the polymer matrix, without additional accumulation on the plastic external surface.[22,23] In this case, molecules are not chemically bound to the microplastic fibers but instead are encapsulated within the polymer chains by intermolecular forces.[24]

Although previous studies have demonstrated leaching of dissolved organic matter and other chemicals from cigarette-related materials,[7,9,10,14] the relative contributions of cigarette tobacco, smoked cigarette filters, unsmoked cigarette filters, and cellulose acetate to leachate composition remain poorly constrained. Also, because most existing studies on cigarette leachates include tobacco, there is limited understanding of how isolated cigarette filters and their components contribute to organic chemical leaching in the absence of tobacco or how sunlight affects chemical composition and leaching rates. This study addresses these gaps by (1) determining how various cigarette filter components contribute to chemical leachates, (2) assessing how simulated sunlight exposure and aging of filters influence leaching dynamics, and (3) investigating how diffusion limitations affect leaching kinetics. To accomplish this, we compared leachates from unsmoked CFs, machine-smoked CFs, and CA by examining UV−vis absorbance and fluorescence spectroscopic properties, DOC, and TDN. To our knowledge, this is the first study to compare leachates from smoked and unsmoked cigarette filters with those from pure cellulose acetate.

2. MATERIALS AND METHODS

2.1. Cigarette Filter and Cellulose Acetate Preparation

Cellulose acetate powder, unsmoked and smoked cigarette filters, and unraveled cigarette filters were used in leaching experiments (Figure 1). Pure CA powder was utilized as a chemical negative control to establish baseline polymer leaching behavior, independent of fiber morphology and plasticizer presence. The commercial cigarette, Marlboro Red, was used for all cigarette filters in this experiment. Unsmoked filters were isolated from new, unused cigarettes. Smoked cigarette butts were provided by Dr. Suzaynn Schick at the University of California, San Francisco. Cigarettes were smoked using a TE-10 smoking machine, where each cigarette was automatically loaded into a wheel, lit, puffed, and ejected. Each cigarette was puffed for 2 s, once a minute, at a volume of 35 cm^3, for a total of 9 min.

All filters were extracted by excising the tobacco portion of the unsmoked cigarette or smoked cigarette butt and removing the wrapping and tipping papers. Unraveled cigarette filters, cut lengthwise and unfurled laterally, were also tested to assess the effect of surface area on leachate diffusion. Pure CA powder was purchased from Sigma-Aldrich (CAS 9004-35-7). For leaching experiments, the average mass of one cigarette filter (0.116 ± 0.009 g, from n = 196 smoked and unsmoked samples measured in this study) was represented by an equivalent mass of CA.

2.2. Leachate Generation

CF and CA leaching batch experiments were conducted in ultrapure water as the leaching solution (salinity: 0.00 parts per trillion (ppt)). For each experiment, three replicate beakers were filled with varying volumes of ultrapure water. Isolated cigarette filter(s) or cellulose acetate were added to each beaker and stirred at 400 rpm. We did not consider the effects of potential abrasion via stirring in this study. Additional equipment information can be found in Supporting Methods S1.

Leaching was conducted under either dark or photoirradiation (simulated sunlight) conditions at circumneutral pH values (7.97 ± 1.05) and ∼ 26 °C. The solution volume, material mass, and environmental conditions varied (Table S3). Data were normalized to account for solution volume and material mass. Leaching experiments spanned either 6 or 24 h. Leaching for 336 h (2 weeks) was also tested to confirm that 24 h was sufficient to capture the leaching kinetics. Subsequent experiments were shortened to 6 h to further maximize efficiency while still allowing adequate time for leaching. Select filters were subjected to a second 24-h leaching cycle, hereafter termed "releaching". Releaching took place 20 days (unsmoked) and 24 days (smoked) after the initial 24-h leaching experiment. Cigarette filters were stored wet in amber vials in a 4 °C refrigerator between initial and releaching experiments. Immediately prior to the releaching experiment, CFs were dried overnight at 30 °C, then reweighed.

Leaching in synthetic stormwater was also performed to test the effect of a higher ionic strength solution (salinity: 0.06 ppt). Smoked

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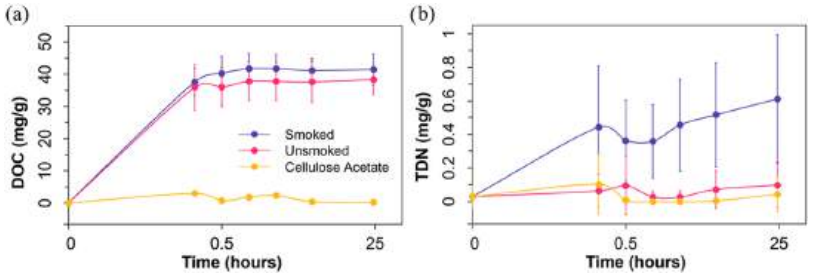

Figure 2. Mean (a) DOC and (b) TDN concentrations (mg/g) leached over 24 h under dark conditions. Error bars represent standard deviations. Table S5 contains data and replicate counts for each time point (n = 3−15). Note the log-transformed x-axis.

and unsmoked CFs were leached in synthetic stormwater (60 mg/L solution of Instant Ocean Sea Salt) under dark conditions.

2.3. Environmental Conditions

The dark environmental condition was created by covering the stir plate and beaker setup with an opaque storage tote. Sunlight exposure was simulated using a SUNTEST CPS+ Solar Simulator equipped with a xenon lamp, daylight reduced IR filter (300−800 nm), and a SUNCOOL chilling unit to maintain the ambient interior chamber temperature. The SUNTEST irradiance was set to simulate the average annual solar intensity in San Diego (longitude 117° 10′, latitude 32° 43′) of 332 W/m^2, calculated from SPEKTRA global irradiance data (Supporting Methods S2).

The effect of sunlight exposure before leaching was also tested. For the dry-aging treatment, the Atlas SUNTEST CPS+ Solar Simulator with SUNCOOL chilling unit was used to irradiate cigarette filters prior to leaching. Filters were placed into sealed quartz tubes to limit air flow. The aging time (7.45 days) was determined from the average dry days between precipitation events, using precipitation data for calendar years 2018−2023 from National Oceanic and Atmospheric Administration (NOAA) station USW00023188, San Diego International Airport.[25] To expedite the aging process, the 7.45-day aging at 332 W/m^2 was achieved by using the maximum irradiance of the solar simulator, 765 W/m^2, for 38 h 47 min, calculated following Hepsø[26] (Supporting Methods S3).

2.4. Chemical Analysis

2.4.1. Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN). DOC and TDN concentrations were measured using a TOC-L TOC analyzer, which uses high-temperature combustion to measure nonpurgeable organic carbon concentration (equivalent to DOC) and chemiluminescence detection to measure total nitrogen concentration (equivalent to TDN) in mg/L. The instrument detection limits (IDL) were calculated to be 0.22 mg/L for DOC and 0.15 mg/L for TDN (Supporting Methods S4). Statistical tests were performed using RStudio. Significance of data at the 95% confidence interval ($p < 0.05$) was determined using one-way ANOVA.

2.4.2. UV−vis Absorbance and Fluorescence Spectroscopy. Fluorescence spectroscopy can be used to detect and quantify aquatic contaminants. The method is widely accepted for characterizing naturally occurring dissolved organic matter (DOM) and has recently been applied to plastic contaminants, including polystyrene, PVC,[17] and tire wear particles.[27] The resulting three-dimensional fluorescence excitation−emission matrix (EEM) spectra of leachates can be used to identify chemical characteristics[28] and track fluorophore quantities over time.

UV−vis absorbance and fluorescence EEMs of leachates were acquired simultaneously using a Horiba Aqualog Fluorometer for excitation wavelengths of 240−450 nm and emission wavelengths of 275−700 at 1 nm increments, using an integration time of 0.5 s. MATLAB was used to normalize the data and generate EEMs, following the methods of Mladenov et al.[29] The resulting EEMs have fluorescence intensities in Raman units (RU) (Supporting Methods S5). A fluorescence peak picking method was used to identify recurring peaks with the highest intensities by visually inspecting EEM spectra and extracting values from the 3D matrices.[30]

Additional optical properties can be used to characterize changes in various attributes of dissolved organic leachates. Specific UV absorbance at 254 nm (SUVA) serves as an indicator of DOM aromaticity, with higher SUVA values correlating to greater aromaticity. SUVA was calculated using the UV−vis absorbance measured at 254 nm (UV_{254}), the DOC concentration (mg/L), and a path length of 0.01 m for the sample quartz cuvette.[31] Spectral slope ratio was calculated per Helms et al. as the ratio of the spectral slope at intervals 275−295 and 350−400 nm. In natural waters, a lower spectral slope ratio correlates with higher molecular weight DOC content. As the fraction of low-molecular-weight DOC increases, so too does the spectral slope ratio.[32]

2.4.3. Kinetics Modeling. A radial diffusion model for cumulative mass release from a cylinder was analyzed for DOC leached from smoked and unsmoked cigarette filters. The model is derived from Fick's second law to describe a concentration gradient-driven process. It assumes a perfect sink scenario with nearly zero diffusant concentration in the surrounding solution, a constant diffusion coefficient of the diffusing species, and constant dimensions (i.e., radius) of the polymer matrix. This radial diffusion model describes molecules that are not chemically bound to the microplastic matrix they inhabit. Their desorption is controlled by internal diffusion within the matrix rather than mass transfer across the aqueous boundary layer.[24,33] The radial diffusion model was originally developed to predict controlled drug delivery.[34] More recently, this model has been applied to the release kinetics of additive flame retardants from microplastics.[23,24] The following approximation equations describe the cumulative mass released as a function of time:

$$\frac{M_t}{M_0} = 4\left(\frac{kt}{\pi}\right)^{1/2} - kt \quad \text{when } \frac{M_t}{M_0} \leq 0.4$$

$$\frac{M_t}{M_0} = 1 - \frac{4}{2.405^2} e^{-2.405^2 kt} \quad \text{when } \frac{M_t}{M_0} > 0.6$$

where M_t is the total mass released after time t (moles or g), M_0 is the mass initially present within the microplastics (moles or g). The original approximation equations were further simplified to combine the unknown diffusion coefficient, D, and cylinder radius, a (m), into a dummy kinetic variable, $k = \frac{D}{a^2}$. Based on our results for DOC concentrations over time, for this model we assumed that all compounds that could be released were released from CFs during these leaching experiments, so we set M_0 to be equal to the DOC concentration after 24 h. Excel's Solver tool was used to determine the value of k that minimized the root-mean-square error (RMSE) of the model.

3. RESULTS AND DISCUSSION

3.1. Release of Carbonaceous and Nitrogenous Compounds from Smoked and Unsmoked CFs

Filter smoking condition significantly influenced the amount of DOC leached under dark conditions ($p < 0.001$). Smoked CFs

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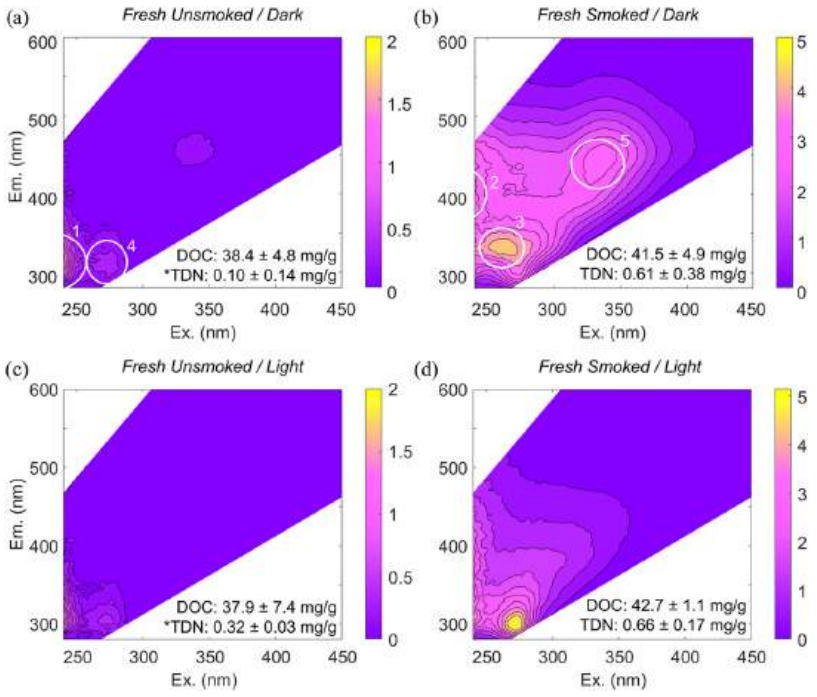

Figure 3. Representative fluorescence EEM spectra for (a) unsmoked CFs and (b) smoked CFs leached for 24 h under dark conditions and for (c) unsmoked CFs and (d) smoked CFs leached for 24 h under photoirradiation. CF-derived fluorescence peaks labeled 1−5. DOC and TDN concentrations (mg/g) provided, and statistically significant differences between dark and light values are shown with an asterisk ($p < 0.05$). Note the differing intensity scale maxima. Peak intensity values provided in Table 1.

leached on average 3.1 mg/g more than unsmoked CFs and ∼167 times more than CA. Within the first hour of leaching, DOC concentrations plateaued at 41.5 ± 4.9 and 38.4 ± 4.8 mg DOC per gram of smoked and unsmoked CF, respectively (n = 15). Pure cellulose acetate, on the other hand, leached negligible quantities of DOC (Figure 2a). Our 24-h leaching results are consistent with a previous study of the effects of chlorination on unsmoked CF leaching, in which the DOC concentration (mg/L) in deionized water appeared to plateau at approximately 42 mg/L (1 CF/100 mL) after 2 days.[35] For direct comparison, the average DOC concentration for unsmoked CF leachates in this study (38.4 ± 4.8 mg/g) converted to 1 CF/100 mL equates to 43.8 mg/L. Our findings here suggest that the DOC leached from CFs is not substantially derived from the CA raw material and originates from an alternative source within the CF.

In our releaching simulations, the same cigarette filters leached 96% less DOC during their second round of leaching than was released during the initial 24 h-setting ($p < 0.001$; Table S4). These observations confirm that carbonaceous compounds are released from CFs very rapidly upon first contact with water. Additionally, our results demonstrate that nearly all leachable organic carbon compounds are released into solution within 24 h. Alberti et al. reported similar findings when leaching smoked and unsmoked full cigarettes, with most DOC released within the first hour and no further change in DOC levels after 24 h.[14]

In contrast to the DOC results, there was a significant difference ($p < 0.001$) between TDN concentrations leached from smoked CFs (0.5 ± 0.3 mg/L) and unsmoked CFs (0.06 ± 0.04 mg/L) after 24 h (n = 15). Unsmoked CFs and CA (0.008 ± 0.019 mg/L) yielded TDN levels below the instrument detection limits (0.15 mg-N/L) (Figure 2b). The disparity suggests that the leached nitrogenous compounds form and attach to the CF fibers during smoking, rather than originating from the cellulose acetate material or from contact with unsmoked tobacco. The higher standard deviations observed for smoked CF leachates are likely due to variable amounts of these nitrogenous combustion products sorbing to the CF fibers.

Richardot et al. identified 43 unique compounds in smoked cigarette butt leachates, 63% of which were aromatic. Of the chemicals they identified, five of the 20 most abundant were tobacco-derived, nitrogen-containing alkaloids: nicotine, anatabine, cotinine, myosmine, and anabasine,[7] which may be responsible for the higher TDN concentrations of smoked CF leachates in this study. Among these compounds, we expect nicotine, which represented ∼ 25% of the compound abundance in Richardot et al.,[7] to also be dominant in the smoked CF leachate. Smoked and unsmoked CF compound identification through targeted and nontargeted chemical analysis is an ongoing line of research in our group.

The dynamics of TDN leaching in this study mirror the first order reaction model of nicotine released in water by smoked cigarette butts.[36] TDN was released rapidly within the first 1−2 h from both smoked and unsmoked CFs (Figure 2b). But unlike DOC, TDN concentrations did not reach an observable plateau during our 24-h or 336-h leaching experiments. This sustained release highlights a key difference in leaching behavior: nitrogenous compounds may continue to leach from smoked cigarette filters for longer than 24 h, while most DOC is leached instantaneously. Consequently, cigarette butts discarded in the environment may serve as a continuous source of nitrogen pollution to waterways.

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Table 1. Common Fluorescence Peaks Identified in Cigarette Filter Leachates in This Study, Their Mean Fluorescence Intensity (RU/g) after 24 h of Leaching, and Similar Fluorescent Peaks Reported in the Literature[a]

			unsmoked CF peak intensities (RU/g)		smoked CF peak intensities (RU/g)		
peak	excitation (nm)	emission (nm)	dark	photoirradiated	dark	photoirradiated	probable sources and peaks found in literature
1*	240	305−345	1.69 ± 0.70	1.24 ± 0.15	5.99 ± 2.36	2.66 ± 0.31$^{\Delta}$	protein (tryptophan)-like: C1,[18] C5,[27] T[28] Phenol-like: C1, C3[17]
2*	240	375−427	0.64 ± 0.46	0.33 ± 0.04	6.16 ± 2.82	2.44 ± 0.31$^{\Delta}$	humic-like: C3,[27] A, M,[28] C2[39]
3*	263	315−335	0.42 ± 0.17	0.25 ± 0.01	6.60 ± 2.68	1.21 ± 0.13$^{\Delta}$	not previously identified in literature or OpenFluor database[40]
4*	273	300−310	0.54 ± 0.26	0.36 ± 0.03	5.30 ± 1.99	1.93 ± 0.17$^{\Delta}$	protein (tyrosine)-like: B[30] Phenol-like: C4[17]
5*	336	440−450	0.20 ± 0.13	0.027 ± 0.005	4.86 ± 2.01	0.26 ± 0.03$^{\Delta}$	nicotine-like: Figure S1b Humic-like: C3,[18] T,[28] C,[30] C1[39]

[a]Asterisk (*) indicates statistically significant ($p < 0.05$) difference between materials. Delta ($^{\Delta}$) indicates statistically significant ($p < 0.05$) difference between light and dark conditions for the given material. $n = 2$ for photoirradiated samples. $n = 14$ for dark samples.

3.2. Aromaticity and Humic DOM Associated with Smoked CF Leachates

Analyses of UV−vis absorbance and fluorescence spectroscopic properties revealed that compounds leached from smoked CFs were more aromatic and higher molecular weight than those released from unsmoked CFs. After 6 h of leaching under dark conditions, smoked CF leachates had significantly higher SUVA than unsmoked CF leachates ($p < 0.001$), which signifies higher aromaticity. The SUVA of smoked CF leachates averaged 0.31 ± 0.03 L/mg-m, while unsmoked averaged 0.079 ± 0.017 L/mg-m (Table S6; $n = 3$). SUVA could not be determined for cellulose acetate since the absorbance was below the fluorometer's detection limits, but we expect it to be close to zero. We recognize that the SUVA values of CF leachates in this study are considerably lower than those of natural waters.[31] However, SUVA values reported here are intended for in-study comparison rather than global comparison to natural DOM sources.

The spectral slope was lower for smoked CF leachates (0.81 ± 0.14) than for unsmoked CF leachates (0.93 ± 0.56) and CA (1.75 ± 0.25) (Table S6), which is consistent with values expected for high molecular weight DOC.[32] Burning tobacco during smoking forms high molecular weight PAHs that then sorb to the cigarette filter fibers.[37] Similarly, we expect tobacco alkaloids to be mainly present in the smoked CF leachates. We suspect that the release of aromatic compounds like PAHs and tobacco alkaloids during leaching accounts for the differences in aromaticity and molecular weight between smoked and unsmoked CF leachates.

Both smoked and unsmoked cigarette filters also leached compounds that exhibited innate fluorescence (Figure 3), whereas pure cellulose acetate leachates did not (Figure S1a). The same five fluorescent peaks were detected in both smoked and unsmoked CF leachates. However, peak 5, which overlaps with the peak of nicotine in water (Figure S1b), was rarely observed in unsmoked CF leachates. Peak 1 (ex. 240 nm/em. 305−345 nm) was the most fluorescent peak in unsmoked CF leachates and was the most visually apparent peak in their EEMs. Peak 1 and peak 4 (ex. 273 nm/em. 300−310 nm) are both in regions typically attributed to protein-like fluorescence[28] but may not represent proteins (Table 1). We expect peaks 1 and 4 to correlate with phenol-like compounds, which also fluoresce in the protein-like region[17] and were previously identified in smoked cigarette butt leachates.[7]

We observed similar temporal trends for fluorescence peak intensities as in DOC over the leaching period. For all peaks, intensity plateaued within the first 5 h, with EEMs appearing virtually indistinguishable throughout the experiment (Figure S2). Since fluorescent compounds are only a fraction of the total DOC,[28] we expected fluorescence to align with the DOC leaching kinetics.

All five CF-derived peaks were significantly more fluorescent in smoked CF leachates than in unsmoked ones at all sample times (Table 1), indicating that they originate from the smoking-related compounds, such as nicotine, sorbed to the smoked filter microfibers. Fluorescence at longer excitation−emission wavelengths correlates with more aromatic and higher-molecular-weight compounds.[28] In our study, those peaks (2 and 5) were substantially more fluorescent for smoked than unsmoked CF leachates. The highest emission peak we identified, Peak 5 (ex. 336 nm/em. 440−450 nm), lies within the humic region associated with soil and plant organic material (i.e., tobacco).[30] We acquired the EEM of nicotine in ultrapure water (Figure S1b) and found that the main fluorescent peak of nicotine overlaps with that of Peak 5. Accordingly, Peak 5 was ∼24 times more intense in smoked than in unsmoked CF leachates, presumably due to the higher nicotine content of smoked cigarette butts.[7] In addition to nicotine, fluorescence in the Peak 5 region may derive from other tobacco alkaloids identified in smoked cigarette butt leachates,[7] which we have not yet analyzed. Parallel factor analysis (PARAFAC) modeling of our large fluorescence data set, a facet of our ongoing research, will separate the entire fluorescence signature into discrete components and help unveil subtle peaks that cannot be detected through human observation.[38]

In our releaching experiments, we observed that all peaks were less fluorescent than in the initial leaching experiments. All peaks exhibited >70% lower fluorescence intensity for smoked CF leachates and >30% lower fluorescence intensity for unsmoked CF leachates during releaching compared to the initial leaching (Figure S3). We observed the most significant difference in peak 5 for unsmoked CF leachates, which was 89.5% less fluorescent in the releaching. Our results suggest that most of the fluorescent organic compounds leach from CFs immediately.

3.3. Effects of Photoirradiation on Leaching of Fresh CFs

Of the materials tested, the smoked filter leachates were the most affected by photoirradiation. Although the final DOC concentrations released from unsmoked ($p = 0.84$) and smoked filters ($p = 0.54$) were similar between photoirradiated and dark leachates, we found that the release rate was slower

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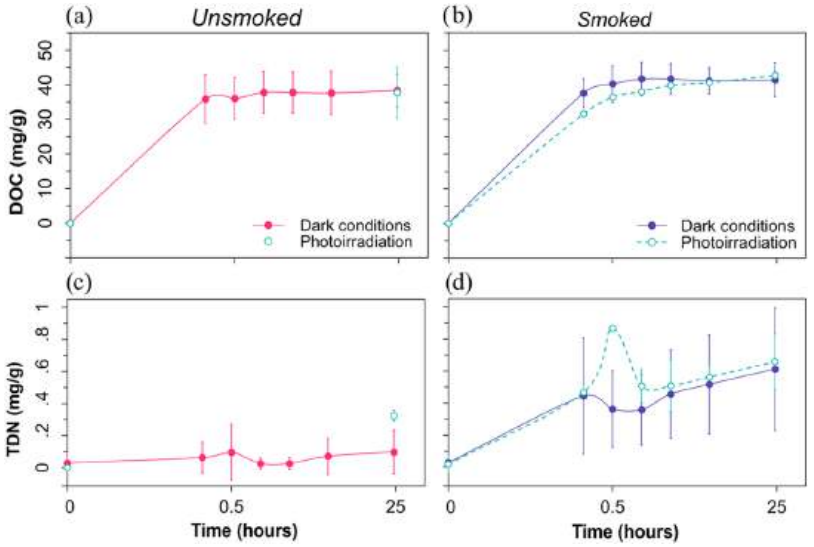

Figure 4. Effect of photoirradiation on mean DOC concentration (mg/g) for (a) unsmoked and (b) smoked CF leachates and mean TDN concentration (mg/g) for (c) unsmoked and (d) smoked CF leachates. Error bars represent standard deviations. Tables S5 and S7 contain data and replicate counts for each time point (n = 2 for photoirradiated and n = 9−15 for dark leachates). Note the log-transformed x-axis.

for smoked CFs leached under photoirradiation than in the dark (Figure 4a,b). DOC for smoked CFs visually plateaued within the first 5 h, which was longer than the 1 h it took to plateau under dark conditions. A two-tailed Mann−Whitney U test confirmed a difference in the time-to-plateau (>95% final concentration) between dark and photoirradiated leachates with a confidence interval of 90% (α = 0.1). The simultaneous phototransformation of leached DOC while it is actively being released would account for the observed slower DOC release under photoirradiation.

Both smoked and unsmoked CFs leached more TDN under photoirradiation than they did in the dark (Figure 4c,d), which suggests that sunlight exposure may exacerbate the release of nitrogenous compounds. Lian et al. demonstrated rapid nicotine phototransformation under simulated sunlight, which was particularly fast in the presence of other organic matter via indirect photolysis. In their photoirradiation experiments, 26% of the nicotine was transformed to more photoresistant compounds (nicotinic acid, cotinine, 3′-hydroxycotinine, and myosmine) within 24 h.[16] Medana et al. further demonstrated that the photodegradation of both nicotine and cotinine resulted in the formation of toxic transformation products.[41]

Additionally, the fluorescence peaks were significantly less intense (p < 0.05) for smoked CF leachates generated under photoirradiation compared to the dark (Table 1 and Figure 3c,d). Of the CF-derived peaks we tracked, humic-like peak 5 was the most photolabile for both smoked and unsmoked CF leachates. After 24 h of leaching, peak 5 was 95% and 86% less intense for smoked and unsmoked leachates, respectively, when generated under photoirradiation as compared to dark conditions. This is consistent with the EEMs we have collected of nicotine in ultrapure water, in which the fluorescence intensity visibly decreased between 10 min and 6 h of photoirradiation (Figures S2c and S2d). Studies indicate that humic DOM is highly susceptible to photolysis,[42] and that natural organic matter is preferentially photodegraded over other aromatic compounds.[43] The decrease in humic-like fluorescence may indicate that tobacco alkaloids are transformed into less aromatic compounds. Lian et al. observed this for nicotine, where they found nicotinic acid to be the most abundant final transformation product.[16]

Peak 3, which has not been previously identified in studies of cigarette leachates or in the OpenFluor database of PARAFAC components,[40] was also relatively photolabile, with photoirradiated leachates being 82% less intense for smoked CF leachates and 40% less intense for unsmoked. Peak 1, the most visually prominent peak observed in unsmoked CF leachates, was the most photoresistant. Increased photoresistance with decreasing emission wavelength has previously been noted for tire wear particle leachates.[27] For smoked CF leachates, peak 1 was significantly less intense for leachates generated under photoirradiation than under dark conditions. This suggests that smoked CFs may have released additional photolabile compounds linked to peak 1, which were not present in the unsmoked CF leachates.

The impact of photoirradiation on SUVA was insignificant for smoked and unsmoked CF leachates after 6 h (p > 0.25; Table S6). However, this may be due to the simultaneous leaching and photodegradation of CF-derived compounds from the CFs in solution. A decline in aromaticity under photo-oxidation has been observed in biodegraded crude oil.[44] The spectral slope ratio increased significantly for smoked CF leachates (p < 0.001; Table S6), denoting a decrease in molecular weight[32] with photoirradiation. Ultimately, the effects of sunlight on CF leachates were most pronounced for the smoked CF leachates, with fluorescence and UV−vis absorbance indices suggesting preferential transformation of humic-like compounds and a decrease in molecular weight.

3.4. Effects of Aging on CFs and Their Leachates

3.4.1. Aging Effects on DOC and TDN Concentrations.

Dry aging prior to leaching resulted in visible color loss and a reduction of tobacco odor, particularly for the smoked CFs (Figure S4). We did not observe any effect of dry aging on the DOC leached under dark conditions. However, aged smoked filters leached significantly less DOC than fresh smoked filters when leached under simulated sunlight (p < 0.001; Table S8). We presume this is due to preferential loss of photolabile organic compounds during aging.

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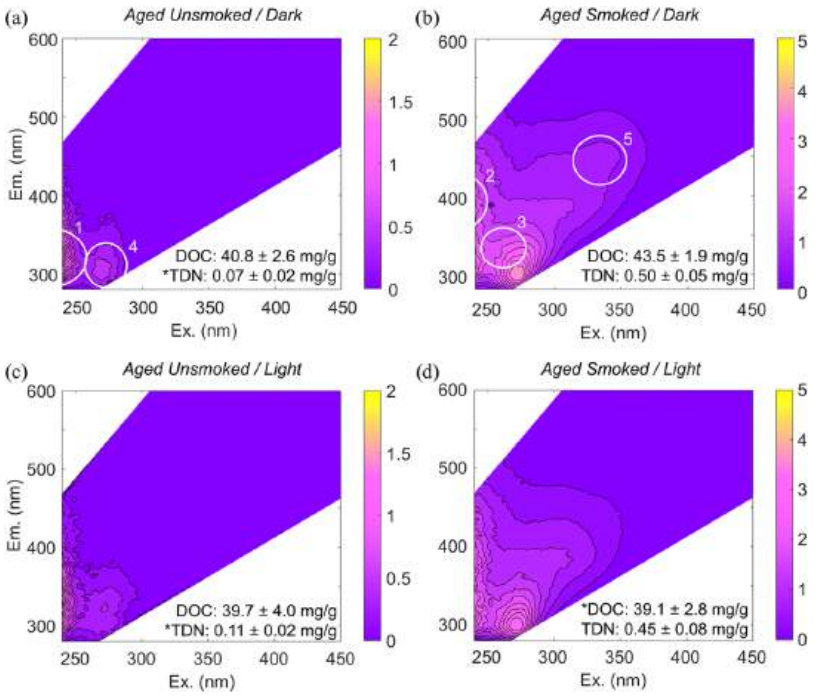

Figure 5. Representative fluorescence EEM spectra for dry-aged (a) unsmoked CFs and (b) smoked CFs leached for 6 h under dark conditions and for dry-aged (c) unsmoked CFs and (d) smoked CFs leached for 6 h under photoirradiation. CF-derived fluorescence peaks labeled 1−5. DOC and TDN concentrations (mg/g) provided, and statistically significant differences between fresh and aged values are shown with an asterisk ($p < 0.05$). Note the differing intensity scale maxima. Peak intensity values provided in Table S10.

TDN leached from smoked CFs was not significantly affected by dry aging. For unsmoked CFs, however, the dry-aged filters leached significantly less TDN than their fresh counterparts under dark conditions ($p = 0.032$). This result would suggest that the aging process removed nitrogenous compounds prior to leaching. When leached under simulated sunlight, aged unsmoked CFs leached significantly more TDN than the fresh CFs ($p = 0.036$; Table S9), which could suggest that aging increases solubility of nitrogenous compounds and their release into solution is stimulated by further sunlight exposure when leached under photoirradiation. However, no previous studies have characterized the leaching of nitrogenous compounds from CFs, so further research is needed to understand these dynamics fully.

3.4.2. Aging Effects on Fluorescence. Aging had a notable influence on the fluorescence intensity of almost all peaks leached under dark conditions (Figure 5, Table S10). For aged smoked CFs, the peaks were significantly less intense for the dry-aged CF leachates than the fresh CF leachates ($p < 0.001$). Peak 3, which appeared only in smoked CFs, was not visible in EEMs after aging (Figure 5), whereas it was a prominent peak in the fresh smoked CFs (Figure 3). This peak may, therefore, represent a compound that is volatile or photolabile in its solid phase.

Peak 5, which we hypothesize to be derived from nicotine and other chemicals in tobacco, appeared in dark leachates of aged and fresh CFs and both smoked and unsmoked CFs. Peak 5 was the only peak that was significantly less intense (~91%) for dry-aged CF leachates than for fresh ($p < 0.001$). These results suggest that photoirradiation during dry aging in the solar simulator removed the peak 5 associated compounds from the dry filter.

All fluorescence peaks of smoked and unsmoked CFs were significantly lower for dry-aged than for fresh filters ($p < 0.001$) when leached under photoirradiation. Peak 5 was photodegraded to near-undetectable levels in dry-aged unsmoked and smoked CF leachates. We believe the high removal of peak 5 with dry aging (>55% for both photoirradiated and dark leachates) indicates that sunlight exposure during aging degraded the fluorescent smoking-derived organic compounds prior to leaching.

3.5. Leaching Kinetics

3.5.1. Assessing Diffusion Limitations. Leaching kinetics were modeled to understand the rate of release of CF-derived chemicals to the environment. We first assessed the controls on leaching, including potential diffusion limitations from solution concentration and chemistry, to determine whether solution saturation would hinder leaching in our experiment configuration. We found that neither solution volume nor CF mass had a significant effect on DOC or TDN concentrations (Tables S11 and S12), resulting in mean concentrations of 41.5 ± 4.9 mg DOC/g CF and 0.5 ± 0.3 mg TDN/g CF after leaching smoked CFs for 24 h under dark conditions. In our experiments, we also observed that the concentration measurements (mg/L) were proportional to the solution volume and the number of filters in the leachate solution. For example, leachates from ten CFs in ultrapure water had roughly ten times the DOC and TDN of one CF in ultrapure water (Table S1). These findings confirmed that the concentration gradient did not limit the leaching of DOC and TDN from cigarette filters in the experiments performed in this study.

Solution chemistry had a notable effect on leaching kinetics. When we conducted leaching in a higher ionic strength synthetic stormwater solution, the CFs leached significantly more ($p < 0.001$; Table S13) DOC in synthetic stormwater (by 27% for smoked CFs), and the release was more gradual

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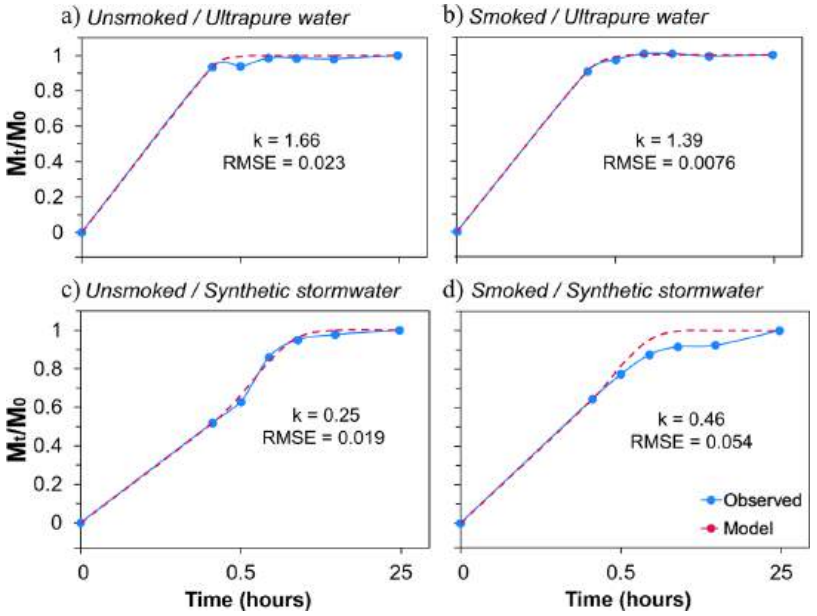

Figure 6. Radial diffusion model projected values of cumulative DOC mass released (M_t/M_0) plotted alongside values calculated for the observed data sets of ultrapure water leachates of (a) unsmoked CFs and (b) smoked CFs and synthetic stormwater leachates of (c) unsmoked CFs and (d) smoked CFs, all leached under dark conditions. Model residuals can be found in Table S14. Note the log-transformed *x*-axis.

than when leaching in ultrapure water. By contrast, TDN concentrations and fluorescent peaks in the higher ionic strength solution were not significantly different from those in the ultrapure water leachates. Salinity affects the solubility of organic compounds in water.[45] Therefore, the changes in DOC dynamics may be due to competitive interactions between anions in the synthetic stormwater solution and the DOM released from the CFs.[46]

Surface area also exerted notable control on leaching. In each triplicate experiment using unraveled CFs, DOC concentration spiked in the first hour of leaching, then rapidly decreased, ultimately stabilizing at the same final concentration as the intact filters. We hypothesize that unraveling amplified the early release of volatile organic compounds by increasing the exposed surface area and enhancing initial contact between the microfibers and water. This likely facilitated the initial rapid release of compounds that were then subject to volatilization. Conversely, the same compounds may have leached more gradually from the intact filters due to slower water infiltration through the compact microfiber matrix. Although volatile compounds were not measured in this study, their presence is being evaluated in our ongoing work using nontargeted chemical analysis. Unraveling also increased TDN concentrations of unsmoked CF leachates, yielding TDN values approximately three times higher than those of intact filters ($p < 0.001$).

3.5.2. Modeling. Previous studies of tire wear particle leaching have found that parabolic diffusion kinetics describe the release of dissolved organic compounds into solution.[47,48] In our work, the data were not well represented by the parabolic diffusion model. Three iterations of the parabolic diffusion model were created via linear regression, plotting varying portions of the data sets as DOC (mg/g) versus $t^{1/2}$ (Figure S5). We normalized the model to M_{24} for direct comparison with the radial diffusion model, yielding RMSE values ranging 0.6−3.4 for ultrapure water leachates.

We therefore evaluated the radial diffusion model, which is based on surface area-derived, cumulative mass release from cylindrical geometry. This model produced much lower errors (RMSE of 0.023 for unsmoked and 0.0076 for smoked CFs in ultrapure water; 0.019 for unsmoked and 0.054 for smoked CFs in synthetic stormwater) and accurately captured the rapid increase and subsequent plateau in DOC concentrations. Although cigarette filter fibers have a trilobal cross-sectional geometry,[49] a cylinder was an appropriate approximation for the diffusion kinetics in this case. Agreement between the model and our experimental data serves as an indication of the underlying kinetics. However, further investigation is required to isolate the diffusion coefficients (D) of the CF leaching. Using an approximate cigarette filter fiber radius of 26 μm, deduced from SEM images from Wilkinson et al.,[2] we estimate the diffusion coefficients of CF leachates are in the realm of 10^{-9} and 10^{-10} m^2/s.

The final model equations for unsmoked CF DOC leachates in ultrapure water were as follows:

$$\frac{M_t}{38.38} = 4\left(\frac{1.66t}{\pi}\right)^{1/2} - 1.66t \quad \text{when } \frac{M_t}{M_0} \le 0.4$$

$$\frac{M_t}{38.38} = 1 - \frac{4}{2.405^2}e^{-2.405^2\times 1.66t} \quad \text{when } \frac{M_t}{M_0} > 0.6$$

The final model equations for smoked CF DOC leachates in ultrapure water were as follows:

$$\frac{M_t}{38.38} = 4\left(\frac{1.39t}{\pi}\right)^{1/2} - 1.39t \quad \text{when } \frac{M_t}{M_0} \le 0.4$$

$$\frac{M_t}{38.38} = 1 - \frac{4}{2.405^2}e^{-2.405^2\times 1.39t} \quad \text{when } \frac{M_t}{M_0} > 0.6$$

The model confirmed that most DOC was released within 1 h, with observed M_t/M_0 values of 1.01 for smoked and 0.99 for unsmoked CFs leached in ultrapure water (Figure 6a,b). In a

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Table 2. Summary of Leaching Characteristics for Smoked and Unsmoked Cigarette Filters

parameter	unsmoked cigarette filters	smoked cigarette filters
	Dissolved Organic Carbon	
DOC concentration	plateau at ∼38.4 ± 4.8 mg DOC g-filter^{-1}	highest release; plateau at ∼41.5 ± 4.9 mg DOC g-filter^{-1}
implied DOC source	primarily filter additives (e.g., plasticizers); not from cellulose acetate	same additive-derived DOC plus minor smoking-related contributions
DOC release timing	rapid; >99% released within ∼1 h	rapid; > 99% released within ∼1 h
effect of sunlight	no significant change in total DOC	no significant change in total DOC; slower release rate
	Total Dissolved Nitrogen	
TDN concentration	very low; near or below detection limits; ∼0.10 ± 0.14 mg N g-filter^{-1} after 24 h	substantially elevated relative to unsmoked filters; ∼0.6 ± 0.4 mg N g-filter^{-1} after 24 h
implied TDN source	minimal; not from cellulose acetate	tobacco combustion residues sorbed to filter during smoking
TDN release timing	mostly within first 1−2 h	continued increasing over time
effect of sunlight	increased TDN release under photoirradiation	increased TDN release under photoirradiation
environmental implication	minor nitrogen source	persistent, long-term nitrogen source to aquatic systems
	Fluorescence Spectroscopy	
overall fluorescence intensity	low to moderate	significantly higher than unsmoked for all peaks
dominant fluorescence types	protein-like and phenol-like components	protein-like, phenol-like, and humic-like components
humic-like peak	weak or rarely observed	peak 5, similar to nicotine ∼24× more intense than unsmoked
effect of sunlight	moderate reduction in fluorescence intensity; humic-like peak highly photolabile	strong reduction in fluorescence intensity; humic-like peak nearly eliminated
effect of releaching	∼96% DOC reduction; >30% fluorescence intensity reduction compared to initial leaching	∼96% DOC reduction; >70% fluorescence intensity reduction compared to initial leaching

similar leaching study, Sun et al. reported much slower release rates from brominated flame-retardant leaching from styrene-type microplastics, compared to the rates we observed for organic compounds leaching from CFs.[23] In their study, compound release from microplastics was driven by the fugacity gradient since flame retardants are added to plastics in such high quantities.[23,24] By contrast, the high kinetic constants in our study likely indicate faster diffusion, potentially resulting from the high aqueous solubility of CF-derived constituents.

The radial diffusion model also assumes that leached compounds are sufficiently hydrophilic to facilitate their rapid release from the solid matrix.[34] One likely CF-derived constituent, triacetin, is considered a highly water-soluble plasticizer (solubility ≈70 g L^{-1} at 25 °C).[50] This solubility is several orders of magnitude greater than any DOC concentration measured in this study, indicating that solubility is unlikely to limit leaching, particularly if triacetin is contributing to the DOC concentration of the CF leachates. Instead, we hypothesize that triacetin's high solubility may facilitate the rapid diffusion of organic compounds from the CF solid matrix.

While the leaching dynamics in synthetic stormwater were more gradual than in ultrapure water (Figure 6c,d), the CFs ultimately leached more DOC in synthetic stormwater after 24 h (Table S13). This enhancement of leaching was unexpected given that the presence of salts typically decreases the solubility of organic compounds in aqueous solutions.[45] This is an important effect and suggests that our results may slightly underestimate the amount of DOC (which is inclusive of organic pollutants) leached from cigarette filters in natural waters. Additionally, while our synthetic stormwater is intended to simulate urban streams influenced by storm runoff,[51,52] replicating our measurements in both sterile-filtered and nonfiltered natural freshwater could provide further insight into cigarette filter leaching dynamics under environmentally relevant conditions.

3.6. Environmental Implications

Trillions of cigarette butts are discarded into the environment annually.[53] The true scale of environmental cigarette pollution is difficult to accurately quantify given the variability in collection methods.[54] Therefore, the urgency to understand their environmental impact continues to grow. Here we show that Marlboro Red cigarette filters, both smoked and unsmoked, are substantial sources of dissolved organic carbon and non-negligible sources of nitrogenous compounds. Given variability of filter additive chemistry between brands, leaching other types of cigarettes may yield different results from those presented by this publication and would require further study. Overall, our findings, summarized in Table 2, indicate that (1) the cellulose acetate polymer itself is not a significant contributor to the organic leachates from commercial CFs, (2) leachate fluorescence and TDN are likely derived from nitrogenous, tobacco-related alkaloids like nicotine that originate during smoking and become trapped in the filter, and (3) the majority of DOC likely originates from additives or plasticizers added to filters during manufacturing.

Leaching dynamics in both ultrapure water and synthetic stormwater revealed that most organic compounds are released from cigarette filters within their first hour of contact with water. This implies that the first rain event after a cigarette butt is littered could trigger significant flux of carbonaceous and nitrogenous dissolved chemicals, such as nicotine, into the environment. Continual TDN leaching observed over longer-term experiments provides evidence that smoked cigarette filters can carry nitrogenous chemicals and continue to release them into water for prolonged periods. Accumulation of cigarette butts on land during periods of dry weather may concentrate the effects of CF leaching at the onset of wet weather. Furthermore, simulated sunlight resulted in photo-transformation, whereby the humic fluorescence of aromatic organics shifted to lower wavelengths, leading to production of new chemicals. Other studies have reported that photo-transformation products of nicotine and cotinine induce

https://doi.org/10.1021/acsestwater.6c00482
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toxicity in model bacteria, even within a few hours of sunlight exposure in water.[41] Therefore, it is essential to reduce cigarette butt waste before it reaches aquatic environments through direct disposal or rain-induced runoff.

Cigarette filters were introduced to create the perception of a safer product, yet they provide no proven health benefits and may even increase certain cancer risks.[3,55] The tobacco industry has also failed to warn that CA filters, which are attached to more than 90% of commercial cigarettes sold globally, are not biodegradable. This misconception has contributed to the littering of trillions of cigarette butts worldwide,[56] generating billions (USD) in waste management costs,[57] and concern for the long-term ecotoxicological effects of this waste. Recognizing this growing environmental problem, the World Health Organization has called for bans on single-use plastic cigarette filters,[58] and some jurisdictions, such as Santa Cruz County, California, have begun implementing such measures.[59] In this study, we show that cigarette filters represent a major source of organic pollutants to the environment. It is currently unknown whether discarded cigarette butts from unfiltered cigarettes exhibit greater or lower ecotoxicity than filtered cigarette butts. However, tobacco, paper, and ash remnants from unfiltered cigarette butts are organic material and thus likely to biodegrade more rapidly. Additional research is needed to evaluate the environmental fate and toxicity of unfiltered cigarette butt waste.

Estimates based on year 2020 cigarette sales and self-reported behavioral data (33−75% filtered cigarette butts discarded into the environment) suggest that between 1.58 and 3.59 trillion cigarette butts enter the environment every year.[53] Based on the DOC and TDN fluxes measured in our study, and the estimated range of butts littered annually, we extrapolate that 7600−17,000 t of dissolved organic carbon and 100−250 t of total dissolved nitrogen enter aquatic ecosystems each year in CF-derived leachate alone. With this study, we advance understanding of the environmental impacts of tobacco product waste and provide evidence to support ongoing efforts to eliminate cigarette filters as single-use plastics that leach toxic chemicals in significant quantities and may lead to yet unknown ecotoxicological impacts.

4. CONCLUSIONS

This study demonstrates that cigarette filters are a significant source of DOC and nitrogen-containing compounds when discarded into aquatic environments. Most organic constituents were released rapidly in both ultrapure water and synthetic stormwater solutions, with the majority of release occurring within the first hour of water contact. This rapid leaching behavior, consistent with a radial diffusion mechanism, suggests that initial rainfall events have the potential to mobilize substantial quantities of filter-derived contaminants into the environment. Our results also show that the cellulose acetate filter material itself exhibited minimal chemical leaching and that most DOC was instead derived from filter additives and plasticizers. Meanwhile, smoked cigarette filters exhibited greater contaminant release than unsmoked filters and continued to leach nitrogenous compounds over extended periods, suggesting their potential to act as persistent sources of pollution. Simulated sunlight exposure altered leachate composition through phototransformation, indicating that discarded cigarette filters may generate secondary compounds after entering the environment.

Taken together, these findings highlight cigarette filters as an important and underrecognized source of organic pollutants in aquatic systems. The nontrivial flux of cigarette filter-derived carbon and nitrogen to aquatic ecosystems further underscores the environmental burden of cigarette butt litter, supports ongoing efforts to reduce its prevalence, and highlights the need for additional research into the long-term ecotoxicological impacts of cigarette filter waste and its transformation products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.6c00482.

Supporting methods including calculations for San Diego irradiance, average antecedent dry days, instrument detection limits (IDL), and EEM normalization; additional tables show global irradiance data, experiment configurations, and experiment data; and additional figures show fluorescence EEM spectra of cellulose acetate and nicotine, additional EEM spectra from cigarette filter leachates, pictures of cigarette filter dry aging, and parabolic diffusion modeling (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Natalie Mladenov − *Water Innovation and Reuse Laboratory, Department of Civil, Construction, and Environmental Engineering, San Diego State University, San Diego, California 92182, United States;* orcid.org/0000-0002-6984-2180; Email: nmladenov@sdsu.edu

Authors

Sarah Poletti − *Water Innovation and Reuse Laboratory, Department of Civil, Construction, and Environmental Engineering, San Diego State University, San Diego, California 92182, United States;* orcid.org/0009-0002-1220-2470

Margaret Stack − *School of Public Health, San Diego State University, San Diego, California 92182, United States; San Diego State University Research Foundation, San Diego, California 92182, United States;* orcid.org/0000-0002-0391-9309

Eunha Hoh − *School of Public Health, San Diego State University, San Diego, California 92182, United States;* orcid.org/0000-0002-4075-040X

George Youssef − *Experimental Mechanics Laboratory, Mechanical Engineering Department, San Diego State University, San Diego, California 92182, United States;* orcid.org/0000-0003-2029-7692

Thomas E. Novotny − *School of Public Health, San Diego State University, San Diego, California 92182, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestwater.6c00482

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Funding for this project was provided by the Tobacco-Related Disease Research Program (TRDRP #T33IR6723) and

TRDRP Supplement to S.P. Additional student support funding was provided by the CSU Council on Ocean Affairs, Science & Technology (COAST) Dr. Kenneth H. Coale Graduate Scholar Award, the San Diego State University College of Graduate Studies, the Carol Forrest, P.E. Memorial Watershed Management Scholarship, and the David G. Fleet Scholarship. The research leading to these results was partly supported by grants from the National Science Foundation (CBET #2327008) and CSU COAST (SSINP-2020-001). We thank Dr. Suzaynn Schick at University of California San Francisco for providing smoked filters. Additional thanks to Dr. Christy Dykstra for guidance on the project and to Jaume Toomer, Marzia Dost, and Ryan Spaulding for laboratory assistance.

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https://doi.org/10.1021/acsestwater.6c00482
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