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Littered cigarette butts as a source of nicotine in urban waters

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SUMMARY

The effect of nicotine from littered cigarette butts on the quality of urban water resources has yet to be investigated. This two-part study addresses the spatial variation, seasonal dynamics and average residence time of littered cigarette butts in public space, as well as the release of nicotine from cigarette butts to run-off in urban areas during its residence time. Thereby, we tested two typical situations: release to standing water in a puddle and release during alternating rainfall and drying. The study took place in Berlin, Germany, a city which completely relies on its own water resources to meet its drinking water demand. Nine typical sites located in a central district, each divided into 20 plots were studied during five sampling periods between May 2012 and February 2013. The nicotine release from standardized cigarette butts prepared with a smoking machine was examined in batch and rainfall experiments.

Littered cigarette butts are unevenly distributed among both sites and plots. The average butt concentration was 2.7 m^{-2} (SD = 0.6 m^{-2}, N = 862); the maximum plot concentration was 48.8 butts m^{-2}. This heterogeneity is caused by preferential littering (gastronomy, entrances, bus stops), redistribution processes such as litter removal (gastronomy, shop owners), and the increased accumulation in plots protected from mechanized street sweeping (tree pits, bicycle stands). No significant seasonal variation of cigarette butt accumulation was observed. On average, cigarette butt accumulation is characterized by a 6 days cadence due to the rhythm and effectiveness of street sweeping (mean weekly butt accumulation rate = 0.18 $m^{-2}\,d^{-1}$; SD = 0.15 m^{-1}). Once the butt is exposed to standing water, elution of nicotine occurs rapidly. Standardized butts released 7.3 mg g^{-1} nicotine in a batch experiment (equivalent to 2.5 mg L^{-1}), 50% of which occurred within the first 27 min. In the rainfall experiment, the cumulative nicotine release from fifteen consecutive precipitation events (each 1.4 mm) was 3.8 mg g^{-1}, with 47% during the first event. According to these results, one cigarette butt may contaminate an amount of 1000 L water to concentrations above the predicted no effect concentration (PNEC) of only 2.4×10^{-3} mg L^{-1} (Valcárcel et al., 2011). Given the continuous littering of cigarette butts, and the rapid release of nicotine, cigarette butts are assessed to be a relevant threat to the quality of urban waters and consequently to drinking water.

1. Introduction

One of the most common elements of urban litter, a cigarette butt, contains a complex mixture of toxins, including the highly water-soluble nicotine. Extremely addictive, nicotine is consumed in massive amounts around the world: 20% of the population over 15 years of age smoke on average 16 cigarettes per day (Giovino et al., 2012). With 73% of the world's population over the age of 14 years (United Nations, online), worldwide an estimated 16 billion cigarettes are consumed daily. With an estimated urbanization of 60% in 2030 (United Nations, online) about 10 billion cigarettes will then be smoked in urban areas every day.

Cigarette butts are the most commonly littered item in urban areas (Bator et al., 2011; Schultz et al., online), making up 22–46% of visible litter, as reported in numerous litter audits worldwide (Schneider et al., 2011; Seco Pon et al., 2012; Moriwaki et al., 2009; Schultz et al., online). Patel et al. (2013) observed that in cities, 76% of cigarettes smoked in public were littered, rather than disposed in appropriate receptacles. The butts are then transported by urban waters to other ecosystems such as coastal areas, where they are consistently the most numerous element of litter collected (International Costal Clean-up, 2013; Ariza et al., 2008). The persistence of cigarette butt filters, made of non-biodegradable cellulose acetate is a concern for wildlife

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(Stanley et al., 1988). Cigarette butts are thus a concern in terms of its environmental, public health, social, and economic consequences (Marais and Armitage, 2004b; Pon et al., 2012; Schultz et al., 2013; Schneider et al., 2011).

Cigarette butts are not evenly distributed in the urban environment. Distribution of butts is linked to the location of sales and consumption. The highest concentrations in the US are associated with bars, convenience stores, liquor stores, cafés, gas stations, grocery stores, restaurants, and traffic signals (Marah and Novotny, 2011). A preference of cigarette smoking has been observed in conjunction with alcohol, coffee, meals, and during breaks, (Van Gucht et al., 2010). Cigarette butts are discarded at places of transition from an outdoor to an indoor environment where smoking is not tolerated, such as entrances to buildings, vehicles or public transportation stations, where the authors found a cigarette butt concentration of 102 m^{-2} in one puddle (see Fig. 1). Non-smoking legislation, in effect in Berlin since 2008, prohibits smoking in the indoor workplace, inside public transit stations and platforms, restaurants, and bars. Since then, it is more common to see an accumulation of smokers outside of restaurant entrances and offices. This phenomenon may well have caused an increase of littered cigarette butts to the urban environment.

The quality of urban run-off is linked to urban litter (Marais et al., 2004a), which in turn is recognized as a major threat to urban water quality (Heinzmann, 1998).

1.1. Nicotine toxicity

Cigarette butts contain a mixture of substances with toxic effects to organisms, most notably heavy metals, polycyclic aromatic compounds, ethyl phenol, and nicotine (Micevska et al., 2006; Moerman and Potts, 2011; Moriwaki et al., 2009). The human toxicological and health effects of nicotine have been extensively studied (Brčić Karačonji, 2005). Nicotine is easily absorbed through the skin, lung alveoli, small intestine, and urinary bladder. It passes easily through the placenta to the fetus.

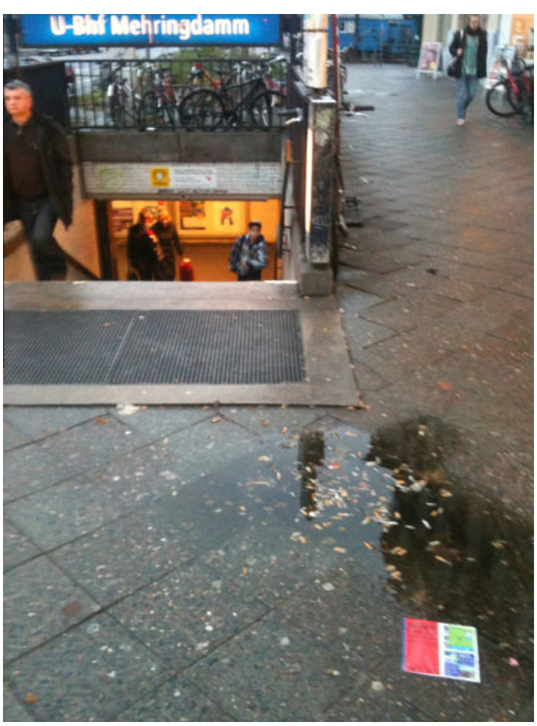

Fig. 1. Typical situation at the entrance of an underground station in detail. Cigarette butt count in the 1.44 m^2 area in the puddle tallied 151. (Photo: T. Nehls, taken on 27.11.2012 in Berlin, Germany).

Strong teratogenic and genotoxic effects have been observed. Nicotine is associated with cardiovascular disease and acts on the central nervous system. Acute toxicity causes death due to paralysis of respiratory muscles or respiratory failure. Nicotine is known to cause liver damage in fish (Konar, 1970), and effects planarians in a similar way as in mammals (Rawls et al., 2011). The effects of chronic sub-lethal concentrations of nicotine and its metabolites in the aquatic environment are not well understood. Based on the EC50 for *Daphnia* of 0.2 mg L^{-1} (Savino and Tanabe, 1989), the calculated value of the predicted no effect concentration (PNEC) for nicotine is 2.4×10^{-3} mg L^{-1} (Valcárcel et al., 2011).

1.2. Nicotine in water resources

Nicotine, and its most important metabolite, cotinine, are important emerging pollutants, widely detected in water resources worldwide in studies of pharmaceutically active compounds (Stuart et al., 2012; Benotti and Brownawell, 2007; Focazio et al., 2008; Valcárcel et al., 2011). Littered cigarette butts have not been examined to date as a source of nicotine in urban waters.

Nicotine has been in use as an insecticide since the 15th century. Because of its toxicity to aquatic organisms, its application has been severely limited in the US, Canada and Europe. Today, nicotine is on the toxic release inventory (TRI) in United States, thus its release into the environment must be reported to state authorities (Environmental Protection Agency, 1996). The European Union classifies tobacco waste as toxic and hazardous when the nicotine content exceeds 0.5 mg g^{-1} dry weight (Civilini et al., 1997). The nicotine content of cigarettes varies according to brand and country of consumption. Between 1998 and 2005, the mean concentration of nicotine in the tobacco rods sold by major manufacturers increased by 9% from 17.1 mg g^{-1} to 18.7 mg g^{-1} in the USA (Connolly et al., 2007).

Nicotine has been identified as one of the three most significant pharmaceuticals with regard to the potential eco-toxicological and toxicological impacts of waste-water treatment plant (WWTP) effluent (Muñoz et al., 2008). In an extensive study of emerging pollutants in Madrid, Spain, nicotine was detected in all river samples downstream from WWTP, with concentrations of up to 1.9×10^{-3} mg L^{-1} (Valcárcel et al., 2011). Leaking septic tanks have been linked to nicotine concentrations of up to 8.1×10^{-3} mg L^{-1} in UK groundwater (Stuart et al., 2012). Nicotine concentrations ranging from 2.5 to 6×10^{-4} mg L^{-1} were observed in estuary water in the US in the proximity of a WWTP (Benotti and Brownawell, 2007).

Nicotine is also found in drinking waters worldwide. An international study in 30 cities reported an average nicotine concentration of 1.9×10^{-5} mg L^{-1} (Boleda et al., 2011). In Madrid, Spain, nicotine was detected in 3 of 5 of tap water samples at levels higher than 4×10^{-6} mg L^{-1} reaching up to 1×10^{-4} mg L^{-1} (Valcárcel et al., 2011). In Miami, USA, concentrations of nicotine of 3×10^{-3} mg L^{-1} have been observed, thus clearly above the PNEC (National Research Council, 1977).

Even in bottled mineral water taken from pristine aquifers, far from anthropogenic sources or sites of tobacco cultivation or production, nicotine was detected in concentrations of up to 1.5×10^{-5} mg L^{-1} (Alonso et al., 2012).

It is important to understand sources, pathways and transformations of nicotine at the numerous natural and technical urban water interfaces (Gessner et al., 2014) and its relevance as an urban water contaminant. As littered cigarette butts may be one of these sources, the aims of the study are:

(i) To analyze the spatial and temporal variation of littered cigarette butt accumulation in Berlin, Germany, and to determine average butt weights and residence times, as well as.

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(ii) To investigate the elution of nicotine from average cigarette butts in average residence times in a batch and a simulated rainfall experiment, simulating elution in standing water and during rainfall and drying cycles.

By combining results from the two studies (iii) we assess if cigarette butts are a significant source of nicotine in surface run-off and surface waters in the urban context. Recommendations for city planners are then discussed.

2. Materials and methods

2.1. Sites and cigarette butt sampling

The study was conducted in Berlin, Germany, with a resident population of 3.5 million, and 9.7 million visits from tourists in 2011. It is estimated that 31% of the Berlin residents are cigarette smokers (Amt für Statistik Berlin-Brandenburg, online), which is higher than the worldwide average. The average population density in the inner-city study area is 11,150 person km^{-2}, the highest among German inner-city areas (Umweltatlas Berlin, online).

Preliminary samplings were conducted in various areas of the city which in part confirmed spatial patterns of littered cigarettes as reported by Marah and Novotny (2011), and from which we derived criteria for site selection. As representativeness is difficult to achieve in urban areas, and because of limited resources, we chose the study area which represented the widest range of land-use types, human impact intensities, and cigarette littering frequencies expected within an inner-city district. Furthermore, the area included combined and separate sewage systems, and open soil, as these features indicate differing nicotine pathways to surface water bodies and groundwater. The city of Berlin relies on water resources from within the city limits for 100% of its drinking water supply.

The inner-city area Treptow–Kreuzberg was identified to be an appropriate fit for the above mentioned criteria. The area is average in relation to socio-economic indicators such as property values, and unemployment rate (fis Berlin, online). The 1.8 km^2 study area includes typical urban land use types such as mixed residential (apartments, town houses), commercial (office space, small businesses like tobacco shops, barber shops), public transport (metro station, train station and bus stops), and a variety of gastronomy types (bistro, restaurant and fast food). The quarter is in close proximity to the receiving urban water bodies, the river Spree and the canal Landwehrkanal. Nine sites with a total sampling area of 1955 m^2 were selected within the study area and were sub-divided into plots (see below). The individual sites were not chosen based on the proportional representativeness of a larger city area. Rather, sites were chosen to represent a wide range of expected littering, from hotspots to sites with very small littering frequency (based on preliminary samplings and observations). The expected high concentration areas included public transit hubs, intensive night-life locations, and office space, while low concentration sites included quiet residential areas with no commercial use, and with low pedestrian frequency. A summary of site information is provided in Table 1.

2.1.1. Plot design

At each site, twenty plots (one site had 21 plots) of variable size >3 m^2 (average 10.8 m^2, N = 181, SE = 0.4 m^2) were demarcated on the sidewalk. The intention of the plot design was to investigate the spatial distribution of cigarette butts according to the features: tree pits (sites 1, 2, 3, 4, 5), bus stops and their waiting areas (sites 1, 7, 8, 9), bike stands, entrances to buildings, shops, or properties (all sites), and gastronomy including restaurants, fast-food stands, convenience stores and bars (sites 1, 5, 6, 8). All features were studied across varying intensities of human impact, and thus cigarette littering. Based on observations, the plots were also demarcated to include site-specific local pockets of high cigarette accumulation in order to assess worst case situations. The variance in the plot sizes is due to the heterogeneity of the studied sites and features. Plots with the feature tree pit contained, in addition to the unpaved area itself, the row of pavement stones bordering the tree pit. All plots adjacent to the street included a 0.1 m strip of the adjoining gutter. The goal of investigating a widest possible range of cigarette butt concentrations, including worst case scenarios, implies a certain sampling bias. However, due to the large number of plots (N = 181), this sampling design is well-suited for an analysis of the spatial patterns and accumulation trends, rather than a representative magnitude for central Berlin.

2.1.2. Sampling scheme

A total of five collections were conducted between May 2012 and February 2013. All sites were investigated for variations in short term (1–3 weeks) and long term (13–17 weeks) accumulation periods, as well as seasonal variation. The accumulation period is defined as the number of days between sampling events in which new cigarette butts are accumulated in the plots. At collections, all identifiable cigarette butts, including damaged or extremely weathered pieces found within plots were removed from the site (sometimes getting pitying looks and fresh cigarettes been offered) and brought to the laboratory. They were then counted, some were dried (50 °C), and weighed (average butt weight of 0.2 g, N = 4,787). Differences in accumulation periods lengths were due to extreme weather situations such as heavy rain, snowstorms, or long periods of remaining ice and snow in which it was impossible to find and collect all cigarette butts from all plots of the sites.

2.1.3. Data analysis – butt collection

Statistical analysis of the data was performed using R software (Version 2.15.2, R Development Core Team). Means of cigarette butt concentrations for the plots were not normally distributed when tested on each sampling (Shapiro–Wilk test $p < 0.05$). As normal distribution was not achieved through data transformation, statistical analysis of the significant difference of the means according to the features described above, was performed using the non-parametric Kruskal Wallis test. Requirements of homogeneity of variances were tested with the Fligner Kileen test. For the features bus stop, entrance, bicycle stand, and gastronomy, only plots containing the feature were counted as such. Features with significant differences in means were compared against one another via plot means, normed over site and sampling. These means, with normal distributions and homogeneous variances, were then tested with ANOVA, and Tukey post hoc tests.

For the analysis of temporal distribution, it was necessary to compare butt accumulation across all sites with differing concentration ranges. Therefore, the site means were normed by the highest plot concentration across all collection periods. The site means were then grouped according to accumulation period and plotted. To analyze the accumulation dynamic of cigarette butts in plots with special features, all plots were grouped by feature, and then the concentrations were normed by the highest plot concentrations over all collection periods in the groups.

2.2. Nicotine elution from cigarette butts

The collections in the city described above were designed to determine the variability and average concentrations, butt weights and residence times, while in the laboratory experiments, described in the following, the nicotine release from average cigarette butts during the resulting residence times was determined.

Table 1
Description of the sites for littered cigarette butts collection in Berlin, Germany.

Site no.	Address	Type of use	Latitude	Longitude	Functional features
1	Lohmühlenplatz	Residential	52°29′21.64″N	13°26′26.27″E	bu, en, ga, tp
2	Lexisstrasse	Residential	52°29′25.48″N	13°26′30.68″E	en, tp
3	Martin-Hoffmann Strasse	Residential	52°29′42.94″N	13°27′26.12″E	en, tp
4	Martin Hoffmann Strasse	Office	52°29′40.57″N	13°27′33.21″E	bst, en, tp
5	Schlesische Strasse	Residential/nightlife	52°29′59.04″N	13°26′39.20″E	bst, en, ga, tp
6	Treptower Park S-Bahn Station	Public transport	52°29′35.69″N	13°27′38.52″E	bst, en, ga
7	Elsenstrasse	Public transport	52°29′32.46″N	13°27′29.37″E	bst, bu, en, tp
8	Schlesische Strasse	Public transport	52°29′51.48″N	13°26′52.80″E	bu, en, ga
9	Reichenberger Strasse	Public transport	52°29′37.23″N	13°26′13.50″E	bu, en, tp

tp – tree pit, unpaved sidewalk vegetation, bu – bus-stop, en – entrance including commercial, residential, office, or fenced yard, ga – gastronomy, bs – bicycle stand.

2.2.1. Preparation of standardized cigarette butts (SCBs)

'Standardized cigarette butts' (SCBs) used in the study were produced in the laboratory from the cigarette brand with the highest worldwide market share (Mackay and Ericksen, 2002) purchased in Berlin, Germany. The nicotine content of this product was close to the mean of all products with over 3% market share in the US (Kozlowski et al., 1998).

The average cigarette butt length of 3.7×10^{-2} m ($N = 124$) was ascertained from freshly discarded cigarettes from an extra sampling campaign which corresponded to a SCB's dry weight of 0.3 g ($N = 8$). All SCBs were smoked to this length with a smoking machine (RM 20/CS; Heinrich Borgwaldt GmbH, Hamburg, Germany) according to ISO 3308:2012 (puff volume: 35 ± 0.3 mL, puff duration: 2 ± 0.05 s, puff frequency: 60 ± 0.5 min^{-1}). Additionally, SCBs with 3, 6, and 7×10^{-2} m length were produced. The SCBs were dried at 50 °C prior to use in the following laboratory experiments.

2.2.2. Batch experiment puddle

In order to study the release of nicotine from cigarette butts, one SCB was added to 1 L of purified water in an amber glass bottle (three replicates). Aliquots of 0.01 L were taken after 0.5, 10, 30, 60, 90, 120, 240, 1440 min, filtered with a 0.45 μm glass fiber membrane (GFM Whatman) and stored at 4 °C before analysis. Prior to sampling, the bottle was inverted two times. This minimal amount of mixing was employed to avoid a physical disintegration of the cigarette butt, and to make the release comparable to the situation in a puddle, thus resulting in a conservative estimation of release. The volume decrease due to sampling was considered in the calculation of concentrations.

In order to investigate the relationship between butt length and the nicotine release, the batch experiment was repeated ($t = 240$ min, see below) with SCB of 3, 6, and 7×10^{-2} m and 0.2, 0.5, 0.6 g respectively. Then the released nicotine was related to the SCB weights and to the tobacco weight in the SCB (cigarette filters alone were 2.1×10^{-2} m and weighed 0.17 g).

2.2.3. Simulated rainfall experiment

Five SCBs were weighed and distributed on a stainless steel tray (0.16 m^2) with a 2% slope (usual sidewalk slope). The tray was mounted on top of a continually logged scale (Fig. 2). The SCBs were exposed to 15 consecutive simulated daily rainfall events with an average flow rate of 0.18 mm min^{-1}, and an average sum of 1.44 mm d^{-1}. This event sum is less than 5% of the precipitation event distribution in Berlin (Nehls et al., 2011), and thus an estimate of the minimum amount of water which comes into contact with littered cigarette butts.

Daily run-off from the tray was collected, and stored in amber glass bottles at 4 °C. After the 15 rainfall events, the SCBs were removed, dried at 50 °C, and weighed. Remaining nicotine was eluted from each SCB in 0.25 L of de-ionized water for 1440 min (sampling described above).

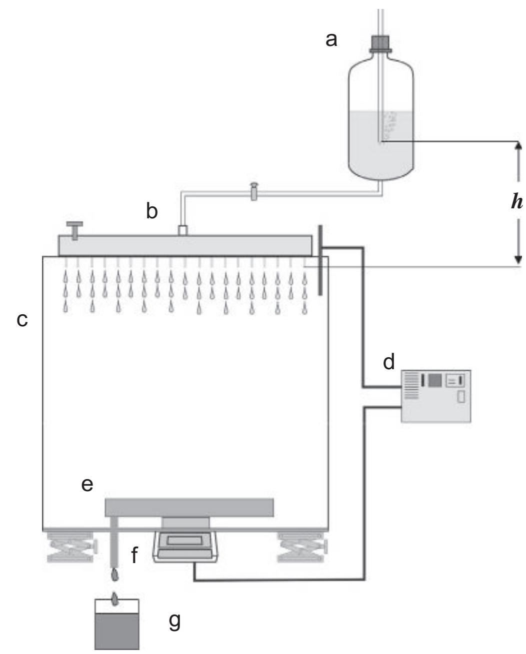

Fig. 2. Experimental setup for the rainfall simulation (a) Mariott's bottle, (b) needle irrigator, (c) hermetically sealed plexiglas box, (d) data logger, (e) stainless steel tray with standardized cigarette butts, (f) digital scale, (g) run-off collection, and (h) pressure difference, adjusted to the targeted rainfall rate.

2.2.4. Analysis of nicotine in water

Nicotine was quantified using LC positive-ESI–MS/MS (HP 1100, Agilent, Waldbronn, Germany; Quattro Micro, Waters). Nicotine was detected in the selected reaction monitoring (SRM) mode. The product ions for the SRM experiments were determined by infusion of nicotine (product ions m/z 117 and 130), and continine-d_3 (product ions m/z 101 and 80) which was used as an internal standard. For both compounds the cone voltage was set to 30 V and the collision energy to 23 V. The pressure in the collision cell was 1.95×10^{-6} bar. Ultrapure water and methanol, both with 1×10^{-3} M ammonium acetate, were used as an eluent for the LC separation The following elution was employed: initial 90% water isocratic for 0.5 min, a linear gradient to 100% methanol within 2.5 min, and then within 0.5 min to 90% water which was isocratic for 16.5 min. The flow was 2.5×10^{-3} L min^{-1} and the column was set to 30 °C.

The compounds were analyzed with 5×10^{-5} L of the internal standard added to 1×10^{-3} L of each sample. The concentration was determined from the peak area ratio of m/z 117 (nicotine) to m/z 80 (continine-d_3). The mass spectrometer was calibrated from 50 to 800×10^{-6} g L^{-1} nicotine with correlation coefficients greater than 0.998. The limit of quantification, determined by preliminary analysis, is 4×10^{-5} g L^{-1} nicotine. All samples were analyzed twice.

Nicotine and continine-d_3 were purchased from Sigma Aldrich. 7.92×10^{-5} L nicotine (density 1.010 g cm^{-3}) was dissolved in 0.1 L ultra pure water, and than diluted to final concentrations of 80, 50, 40, 20, 10 and 5×10^{-2} mg L^{-1}. Continine-d_3 (1 g L^{-1} in methanol) was diluted to the final concentration of 1×10^{-3} g L^{-1} with ultrapure water. The ultrapure water was produced from de-ionized water with a water purification system (maxima ultrapure water; Elga, Upstadt-Weiher, Germany). All other chemicals used (methanol, ammonium acetate) were LC–MS quality.

3. Results and discussion

3.1. Spatial variation of littered cigarette butts in Berlin

The mean butt concentration over all collections and sites is 2.7 m^{-2} (SD = 0.64 m^{-1}, $N = 862$ sampled plots). The lowest site mean, 0.29 m^{-2} (SD = 0.15 m^{-2}), was observed at site No. 2, a quiet residential side street, with a low pedestrian frequency, as well as an absence of any businesses or public transit stops. The highest mean, 5.2 m^{-2} (SD = 2.2 m^{-2}), was observed at site No. 6, at the main entrance to a well-frequented city train station, including convenience stores, fast food, and bicycle stands.

The spatial distribution of cigarette butts is characterized by pockets of high concentration, on all scales (within the study area, within sites and within plots). Thus, all sites are characterized by a similar right skewed frequency distribution of plot concentrations (Fig. 3). The highest concentration of littered cigarette butts in a single plot was found in site No. 6 near a train station entrance with 48 m^{-2}. That corresponds to a number of 581 butts, almost all of which were concentrated in a large pile of snow. This is an exceptionally high number, most probably containing butts, which were transferred from other plots, or from areas outside the study site. This data has been included in the analysis as it depicts an observed concentration in one plot. This number is relevant for the ecological effects of cigarette butts, regardless of whether the cigarette butts were originally discarded there, or transported through snow removal and sweeping at a later point. Accordingly, individual plot concentrations are up to 500 times higher than the respective mean (Fig. 3). Effects such as wind, water, pedestrians, street sweeping, or snow removal, as well as preferential littering, lead to very heterogeneous distributions of butts in certain plots. There will always be limited certainty as a dynamic system like the city may change while being sampled.

The means of plot concentrations grouped by features are significantly different for all samplings (Kruskal Wallis of normed plot concentrations, $p < 0.05$). The Tukey post hoc test showed that only tree pits contain significantly more (2.9 times more) littered cigarette butts than the control plots with none of the special features (Fig. 4). Tree pits are not cleaned regularly by mechanized street sweeping. Whether butts are preferentially littered to tree pits or the concentration is enriched relative to the surrounding area is not clear. That cigarette butts are removed from other plots and put into tree pits by the sweeping cannot be excluded.

The cigarette butt concentration in bus stops is not significantly lower than in tree pits. Although it is 1.9 times higher than in control plots, that difference is not significant. In winter, when people use public transit more frequently, we observed a trend of higher concentrations. The feature bus stop was not mentioned as a cigarette butt accumulation hotspot in a US American study (Marah and Novotny, 2011). Public transport is more important in Germany, and thus it explains spatial distribution of urban litter to a higher extent than in the USA.

Bicycle stands seem to be protected from sweeping in the same way as tree pits. Means of normed butt concentrations are 1.5 times higher than that of the control plots. The predominant group of bicycle stands was located in site No. 6 near the entrance to a city train station. This uncovered bicycle parking area was not well maintained, and contained a large amount of garbage, fallen leaves, and abandoned bicycles. Littering rates are known to be higher in areas where litter is already present (Schultz et al., 2013). The plot concentrations of the bicycle stands in site No. 6 were especially high for the last winter collection, in which snow had been pushed into large piles.

The feature gastronomy includes restaurants, a fast-food stand, a convenience store, and bars. Therefore it includes many of the types of land use associated with increased butt concentrations in the study from Marah and Novotny (2011). Our results do not show this feature to be the most important indicator of butt concentrations. We observed that not all of the business owners sweep the area in front of their business on a daily basis. Some proprietors dispose the butts properly, while others sweep the butts into the gutters or tree pits. Thus, heterogeneous sweeping activities change the spatial patterns of littered cigarettes leading to both higher accumulation in specific areas, as well as a lower accumulation due to the removal of cigarette butts from the street into properly treated waste streams.

Most probably for the same reasons, plots with the feature ‘entrance’ did not differ at all from the control plots when analyzed

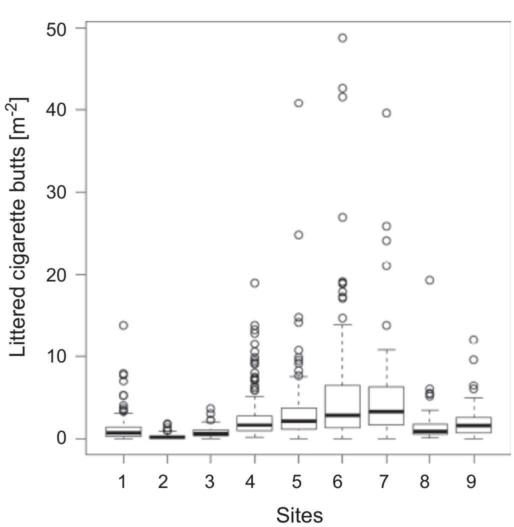

Fig. 3. Concentration of littered cigarette butts for all samplings in all plots of sites 1–9, Berlin, Germany.

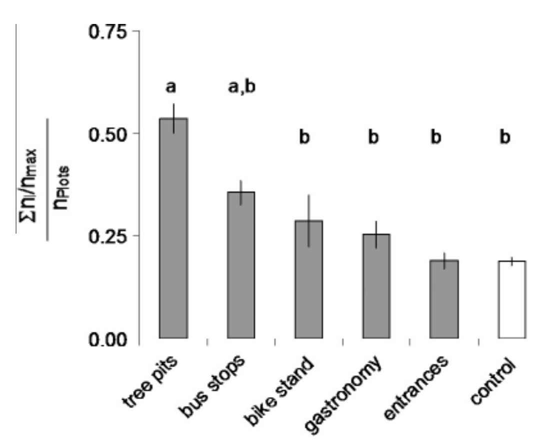

Fig. 4. Concentrations of littered cigarette butts normed by the highest concentration per site, and grouped by functional features. Columns depict arithmetic means, error bars depict the standard error. Bars labeled by the same letter are not significantly different ($p < 0.05$, $N = 181$ plots).

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across all samplings and sites. The feature entrances, like the feature gastronomy, are composed of a non-homogenous group of plots next to a doorway, gated yard, or an entrance to a train station. Some plots were located at entrances to small businesses such as a hairdresser, or a driving school. The workers in these businesses were observed to smoke outside their workplaces during breaks. The high numbers of cigarette butts collected in site No. 4, are due to the entrance to an office space, where many employees take their breaks outside with a cigarette. Although people toss cigarettes before going back to work, they do not necessarily drop the cigarette butt directly at the entrance. Butts can be flicked wide distances away from entrances, or dropped some meters in front of the entrance.

Furthermore, we observed that cigarette butts tend to accumulate in large or uneven pavement joints, such as in cobblestone pavements. In smooth pavement with narrow joints, fewer cigarette butts accumulate.

3.2. Temporal variation of littered cigarette butts in Berlin

Cigarette butts are continually littered into the urban environment. A seasonal variation was not significantly indicated from our samplings. This finding corresponds with other studies on urban litter (Seco Pon et al., 2012). There was also no difference in cigarette butt concentrations between short and long term accumulation periods, exemplified by the oscillating pattern of the temporal variation in Fig. 5a. Despite the great variability between the plots, the average residence time over all sites is six days, as derived by analyzing the phases in which the number of butts increased (5, 4, 6, 6, 9 days). This corresponds to the sweeping frequency by municipal agencies which – depending on the site – varies from a weekly to a daily rhythm (such as at the train station, Berliner Stadtreinigung GmbH, personal information and own observation). Some business owners, as discussed above, also sweep on a daily basis, thus we conclude a minimum accumulation period or residence time of littered cigarette butts of one day. On average, littered cigarette butt accumulation is characterized by a six days cadence with an average butt accumulation rate of 0.18 m^{-2} d^{-1}; SD = 0.15 m^{-1} d^{-1}.

For the feature tree pit (Fig. 5b), there is a trend of higher accumulation with larger sampling intervals. The accumulation periods are longer than for all plots. Thorough cleaning by manual municipal sweeping occurs a few times per year, resulting in the removal of almost all butts in tree pits and bike stands (Berliner Stadtreinigung GmbH, personal information).

Furthermore cigarette butts are littered continuously, but they are not littered consistently. Some areas will experience littering during working hours, as in areas outside of offices, schools, or small businesses, while other areas will see more littering on weekends and at night.

We conclude that the distribution of butts is characterized by site specific short term patterns of increase and decrease due to littering, weathering, erosion, removal and re-distribution with a minimum residence time of one day. The dynamic of nicotine release from a littered cigarette butt is discussed in the following section.

3.3. Nicotine release from standard cigarette butts

The batch experiment is a realistic description of the elution dynamic when cigarette butts come into contact with standing water, including permanent bodies of water such as a lake or a river, but also puddles in street or sidewalk depressions caused by precipitation. In the batch experiment, 7.1 mg g^{-1} (SD = 0.07 mg g^{-1}) nicotine was released from the SCB after 1440 min, 50% of the total amount after 27.2 min and 90% already after 651 min (Fig. 6a). The released concentration after 1440 min is therefore considered to be the total releasable nicotine from SCBs for the rainfall experiment. Nicotine is released quickly to the water phase, according to a first order reaction model $C_L = 0.98 \ln(t) + 0.65$ ($R^2 = 0.94$) with C_L the soluble nicotine concentration (mg g^{-1}) and t the reaction time (min).

Surprisingly, the nicotine release (mg g^{-1}) from cigarette butts increases according to butt weight M_{SCB} ($C_L = 19\ M_{SCB} + 0.5$; $R^2 = 0.92$). This is due to the fact, that the nicotine release from the butt is determined by the remaining tobacco (constant at 16.2 mg g^{-1} tobacco; SD = 1.6 mg g^{-1}, $N = 12$) instead of the filter (0.22 mg g^{-1} filter).

The water-extractable amount of nicotine from a SCB is 14 times higher than the threshold established by the European Union for hazardous tobacco waste (0.5 mg g^{-1}) (Civilini et al., 1997).

From such puddles, nicotine may enter the groundwater, from which drinking water is extracted in Berlin. The filtration capacity of paved soils is decreased depending on the pavement and sub-soil permeability function, as well as the susceptibility to preferential flow, (Nehls et al., 2008). Nicotinophilic micro-organisms

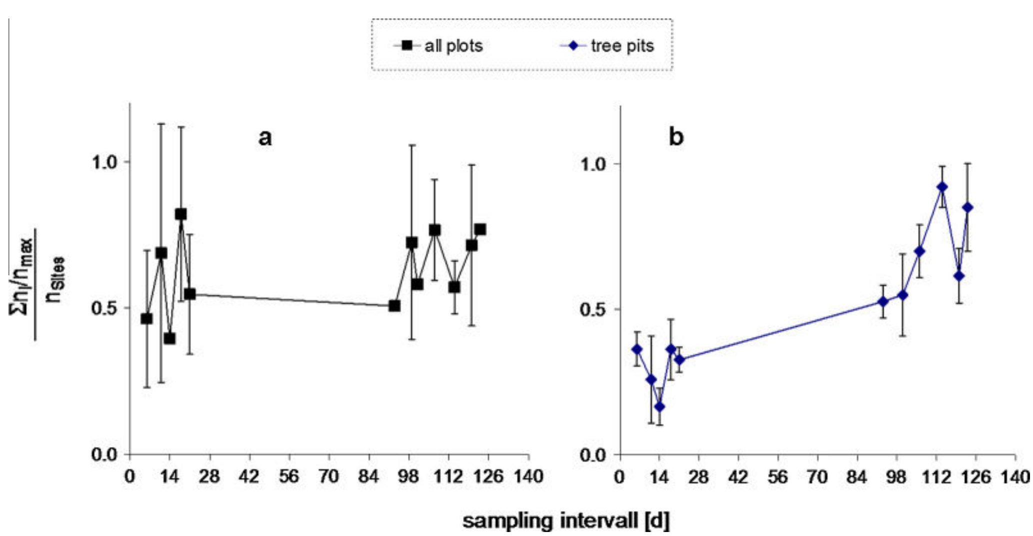

Fig. 5. (a) Concentrations of littered cigarette butts normed by the highest value for the site in all samplings in relation to the sampling intervals for all plots (N = 862 plots) and (b) plots with tree pits. Squares and diamonds depict arithmetic means, error bars depict standard errors (N = 102 plots).

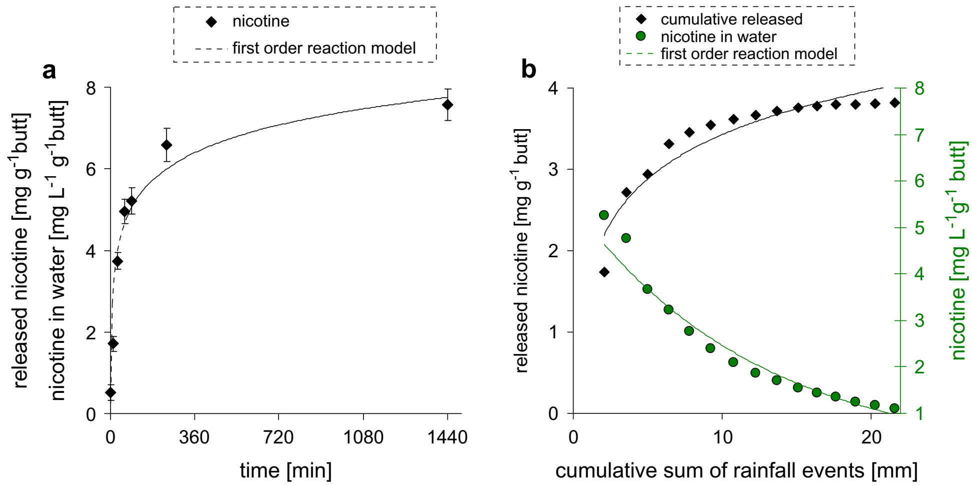

Fig. 6. (a) Dynamic of nicotine release from standardized cigarette butts to water in batch experiments and (b) dynamic of nicotine release from standard cigarette butts to water in a series of simulated rainfall events in the laboratory (right). Circles and diamonds depict arithmetic means, error bars depict standard errors ($N = 3$).

capable of nicotine degradation in water (Civilini et al., 1997) and soils (Ma et al., 2012) have been identified. The existence and activity of such micro-organisms in the particular environment of pavement joint soils (Nehls et al., 2006) have not yet been investigated.

Standing water is common in historic quarters of cities, but not the rule. Therefore, we also tested the elution of nicotine from butts exposed to rainfall without puddle formation.

In the simulated rainfall experiment, the cumulative total nicotine elution from SCBs was 3.8 mg g^{-1} from a total precipitation of 21.6 mm in fifteen events (Fig. 6b). Half of the nicotine was eluted after 1.6 mm or 1.1 events. Again, a first order reaction model provides a good description of the elution dynamic: $C_L = 0.79\ \mathrm{Ln}(P) + 1.62$ ($R^2 = 0.90$), with P the sum of rainfall [mm]. Based on the results of the batch experiment, we recovered a sum of 55% of the total water-extractable nicotine in the SCB's. The remaining amount of nicotine in the SCBs after the 15 rainfall events was 0.16 mg g^{-1} (SD = 0.02 mg g^{-1}; $N = 5$). It can be concluded, that even cigarettes, which were exposed to several precipitation events (in our case seven events) must be classified as hazardous waste.

The measured nicotine concentrations in the run-off water reached up to 5.3 mg L^{-1} g^{-1} SBC. Applied to the mean butt concentration of the study area, nicotine concentrations in the run-off are estimated to reach 0.62 mg L^{-1} (1.44 mm rain event, run-off coefficient = 1). Local concentrations can be as high as 11.4 mg L^{-1} calculated using the highest observed plot concentration. Both concentrations are far above the PNEC, (2.4×10^{-3} mg L^{-1}) (Valcárcel et al., 2011), as well as the EC50 for *Daphnia* (0.2 mg L^{-1}) (Savino and Tanabe, 1989). As cigarette butts are continuously and copiously littered in the urban environment, and given the rapid elution, every precipitation event will release relevant amounts of nicotine into the urban environment. The high local concentrations in hot spots can lead to nicotine flushes, a concern for aquatic ecosystems. Obviously, nicotine concentrations in surface run-off may be extreme for small rain events. Surface run-off draining to separate sewer systems leads directly into surface water bodies without treatment. Effluent from WWTP and leaking septic systems are assumed to be the main source of nicotine contamination in surface and ground water. As nicotine elimination in WWTP has been observed at rates of 75–99% efficiency (Huerta-Fontela et al., 2008), the contribution of nicotine from paved urban areas should be considered as a source of nicotine in surface waters.

While the reported data and calculations are based on experimental study of one common cigarette brand, real-world cigarette litter consists of a mixture of brands and products with varying nicotine content. As more nicotine is contained in the tobacco than in the filter of cigarette butts, the released nicotine depends on the behavior of smokers with regard to littered butt length (weight, filter to tobacco ratio). Likewise, littering habits depend on cultural and socio-economic factors beyond the scope of this study. Consequently nicotine elution will vary due to the local preferences of smokers, as well as the behavior (littering and sweeping) of residents and municipalities. Herein lays the key to cope with the problem!

4. Conclusions and implications for city planning

This study demonstrates that (i) cigarette butts accumulate in high numbers in urban areas and (ii) the nicotine which is released from such litter poses a significant threat to urban water resources. Cigarette butts are continuously littered into the urban environment, and accumulate in areas where they are not regularly removed by private or municipal actors (e.g. tree pits). First flush events with high nicotine concentrations are likely to take place after longer accumulation periods with dry weather. Each littered cigarette butt can potentially release nicotine in concentrations higher than the threshold value of hazardous and toxic waste defined by the European Union. Having its nicotine fully released to standing water, only one cigarette butt can contaminate an amount of 1000 L water to concentrations above the predicted no effect concentration (PNEC) of only 2.4×10^{-3} mg L^{-1} (Valcárcel et al., 2011).

Thus, municipalities have a legal obligation to make sure that this tobacco waste is disposed in an appropriate way. One approach, suggested by Novotny et al. (2009), is to hold cigarette companies legally responsible. Regardless of legal or financial responsibility, management of cigarette butt littering in cities must be implemented.

Although a more effective and frequent street sweeping would help to reduce the released amount of nicotine, our study shows that the present system is already effective where it reaches the litter. It is questionable, if higher frequencies of mechanized street sweeping would change the situation in the high accumulation pockets significantly.

Increasing the number of public ashtrays in areas with high cigarette butt concentrations, such as near well-frequented areas, and bus stops, could reduce cigarette butt littering. Although public ashtrays are already installed on top of the numerous public trash receptacles in the city of Berlin, cigarette butts are littered in large amounts. Furthermore, contradictory results suggest that the effect of ashtrays on cigarette littering rates is not clear (Schultz et al., 2013, Bator et al., 2011; Patel et al., 2013). Nevertheless, intensified street sweeping efforts and the installation of additional ash trays will be an economic hurdle for cities or tobacco companies (Novotny and Zhao, 1999), with unclear effects.

Instead, we recommend a public education approach aimed at effecting a change in littering behavior through awareness-raising. People who consider cigarette butts to be litter are significantly more likely to dispose of their butts properly (Rath et al., 2012). The main message of such a campaign should focus on the toxic nature of cigarette butt waste and the effect on environment and drinking water quality.

Additionally, the pathways of nicotine released from cigarette butts to urban waters are in need of investigation. We recommend the implementation of a monitoring system for nicotine in urban waters (surface, ground- and drinking waters). Furthermore, studies are necessary to observe nicotine not only in surface run-off but for all pathways and transformations it may undergo at natural, technical and natural–technical interfaces such as soil, pavement, sewer, surface water body or WWTP and then surface water, bank filtration, infiltration into groundwater, groundwater extraction, drinking water treatment, drinking water, bottled water (Gessner et al., 2014).

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