



UV-254 degradation of nicotine in natural waters and leachates produced from cigarette butts and heat-not-burn tobacco products

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ABSTRACT

Nicotine is an important emerging contaminant widely detected in water resources. The main nicotine sources are human excretions from users and leaching from discarded tobacco product waste, which represents the most commonly littered item in urban areas and coasts. In this study, the UV₂₅₄ photolytical fate of nicotine in natural water and leachates produced from conventional cigarettes (CCs) and the new generation heat-not-burn (HnBs) tobacco products is examined for the first time. The effect of UV₂₅₄ irradiation on nicotine depletion in ultrapure water was initially studied. The reaction was pseudo first-order with respect to nicotine concentration at low concentrations and shifted to lower order at higher concentrations, an effect associated to absorption saturation. Although nicotine removal was fast, only 9.5% of the total organic carbon was removed after irradiation due to the formation of by-products. The chemical structures of six photo-products were derived by means of liquid and gas chromatography coupled to mass spectrometry. The photodegradation kinetics was found to depend on pH and faster kinetics were recorded when the monoprotonated form of nicotine was dominant (pH = 5–8). The presence of humic acids was found to slightly delay kinetics as they competed with nicotine for lamp irradiance, whereas the presence of salt had no effect on the direct photolysis of nicotine. Direct photolysis studies were also performed using natural waters. Compared to ultra-pure water, photodegradation was found to proceed slightly slower in river water, in similar kinetics in seawater, and relatively faster in rain water. The later was assumed to be due to the lower pH compared to the rest of the natural water tested. Leachates from used HnBs and smoked CCs were also submitted to UV₂₅₄ irradiation and direct photolysis was found to proceed fast despite the high complexity of these matrices. Nonetheless, the total organic carbon in the system remained the same after irradiation due to the abundance of organics and photo-products formed. We take advantage of the present investigations and report the leaching behavior of nicotine from HnBs and CCs. Among others, we found that in HnBs ~70% of the total and bioavailable nicotine content remains in the tobacco sticks after operation and this percentage drops to 15% in CCs due to the reduction in mass after smoking. This finding demonstrated the importance of properly disposing tobacco product waste to prevent nicotine leaching in water bodies.

1. Introduction

Nicotine is a toxic alkaloid found in the tobacco plant (lethal dose for adults is 60 mg (Mayer, 2014)) and the most important component in tobacco products (Buerge et al., 2008). The vast consumption of tobacco products resulted in the widespread nicotine contamination in surface water, wastewater (Buerge et al., 2008; González Alonso et al., 2012; Roder Green et al., 2014) and bottled mineral water (González Alonso et al., 2012), and the classification of nicotine as an important emerging

pollutant (de Granda-Orive et al., 2018; Oropesa et al., 2017). Once consumed, nicotine is extensively metabolized in the human liver by oxidative enzymatic transformations to a number of compounds, and excreted, mostly in the urine, as a complex mixture of the parent compound and its transformation products (Senta et al., 2015). In this connection, nicotine is frequently detected in wastewaters at a $\mu\text{g L}^{-1}$ concentration level, and together with its derivatives are used as anthropogenic markers for urban wastewater contamination and for the assessment of population size and dynamics (Buerge et al., 2008;

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Huerta-Fontela et al., 2008; Senta et al., 2015). Next to wastewater discharges, another important source of nicotine contamination is leaching from smoked cigarette butts (Oropesa et al., 2017; Roder Green et al., 2014). Indeed, the majority of the 16 billion cigarettes consumed daily are being thrown away rather than properly disposed in receptacles (Roder Green et al., 2014). This makes cigarette butts the most widespread and numerous littered item found in urban areas and coasts (Araújo and Costa, 2019; Dobaradaran et al., 2020; Marah and Novotny, 2011; Roder Green et al., 2014; Torkashvand et al., 2020). Today, there is conclusive evidence that when this type of waste comes into contact with water, a number of inorganic (Cardoso et al., 2018; Chevalier et al., 2018; Koutela et al., 2020; Moerman and Potts, 2011; Moriwaki et al., 2009) and organic (Dobaradaran et al., 2019, 2020) compounds, including nicotine (Roder Green et al., 2014), are leached and become bioavailable to aquatic life (Cardoso et al., 2018; Chevalier et al., 2018; Dobaradaran et al., 2020; Koutela et al., 2020; Moerman and Potts, 2011; Moriwaki et al., 2009; Roder Green et al., 2014).

The heat-not-burn (HnBs) tobacco products were recently developed to provide the user with nicotine by heating specially designed tobacco sticks at 350 °C, well below the temperature required in conventional cigarettes (CCs) for initiating combustion (Schaller et al., 2016). Today, HnBs represent the new generation of tobacco products and a fast-expanding market. However, there is a justified fear that improperly disposed HnBs may also have a negative environmental impact through leaching of its chemical components (Baran et al., 2020; Koutela et al., 2020). Although the release of nicotine from CCs has been reported in the past (Roder Green et al., 2014), there are no relevant studies for HnBs. This is of particular importance since in HnBs there is no mass reduction after operation (as seen in CCs where ash is produced during smoking) and as such, HnBs have the potential to release larger amounts of nicotine in water bodies when improperly discarded in the environment.

The transformation of organics (including nicotine) in water is a complex process, and includes biotic and abiotic transformation reactions (Lian et al., 2017; Medana et al., 2016; Passananti et al., 2014). In particular, photochemical reactions may be a major abiotic transformation pathway and can take place *via* direct and indirect photolysis mechanisms (Carena et al., 2020). Direct photolysis refers to the transformation of a molecule upon direct light absorption, *i.e.* the parent compound absorbs irradiation, reach excited molecular states and then undergo chemical transformation (Katagi, 2018). The direct photolysis of a molecule can be inhibited by competitive light-absorbing compounds, including the dissolved organic matter (DOM) that naturally occurs in surface waters (Carena et al., 2020). At the same time, DOM (and/or NO₃⁻) may also act as photosensitizers and trigger the indirect photodegradation of water pollutants with photogenerated reactive oxygen species (Katagi, 2018). Nicotine was previously reported to undergo direct and indirect photolysis at different rates, depending on the conditions (Nienow et al., 2009; Passananti et al., 2014). In particular, indirect photodegradation was found to play a key role in sunlit surface waters (Passananti et al., 2014) and wastewaters (Lian et al., 2017). These studies concluded that nicotine transformation under simulated solar irradiation followed a pseudo-first-order rate reaction (Lian et al., 2017; Passananti et al., 2014), and showed that direct photolysis was non-significant due to the small overlap of the ultra-violet-visible spectrum between nicotine and solar irradiation. In another report, the indirect photolysis of nicotine was investigated in the presence of different naturally occurring photochemical sources of HO• and of nitrogen-centered radicals (Passananti et al., 2014). The second-order kinetic constants of nicotine with HO• and ¹O₂ were determined, and allowed predicting environmental half-life times for such reactions as a function of the water chemistry and depth. In the same report, modelling studies showed that the photochemical half-life of nicotine would vary in the month-year range depending on the environmental conditions. The indirect photolysis of aqueous nicotine in ultra-pure water at λ = 254 nm has also been reported within the frame

of reporting a new H₂O₂-enhanced photodegradation process (Nienow et al., 2009). In this study, a preliminary set of experiments monitored the direct photolysis of nicotine in the absence of H₂O₂ and reported a fast nicotine degradation rate under UV₂₅₄. Based on the published results so far, there is no in-depth study on the direct photolysis of nicotine in aqueous solutions and natural waters; a knowledge indispensable for evaluating the basic photochemistry of nicotine in the aquatic environment. It is equally important that there are no reports studying the photolysis of nicotine in leachates produced from tobacco products, an important type of waste that represents a major nicotine source in the aquatic environment.

The aim of this work was to study for the first time the photolysis of nicotine in natural waters and water leachates produced from CCs and the new generation HnBs tobacco products. Initially, water samples spiked with nicotine were irradiated by UV₂₅₄, degradation rates were recorded and the reaction mechanisms were investigated. The effects of different experimental parameters (pH, effect of salt and humic acids) were then studied in separate sets of experiments. Building on this knowledge, the effect of matrix on nicotine photolysis fate was studied using natural water as leachant (rain, seawater and river water). Finally, the photodegradation of nicotine by UV₂₅₄ was monitored in highly complex leachates produced from used HnBs and smoked CCs, yielding new knowledge on the fate of nicotine under a more realistic scenario.

2. Material and methods

2.1. Chemicals and natural water samples

(–) Nicotine PESTANAL® was purchased from Supelco (Bellefonte, USA). Acetonitrile for LC/MS was obtained from Carlo Erba Reagents (Sabadell, Spain) and formic acid from Fluka Chemie GmbH (Bucks, Switzerland). Sodium chloride (99.9% purity), humic acid, ammonium acetate (≥90% purity) and tert-butanol (≥99% purity) from Fisher Scientific UK Ltd (Loughborough, UK). Acetic acid (100% anhydrous GR for analysis) and boric acid (99.8% purity) were supplied by Merck KGaA (Darmstadt, Germany), potassium phosphate dibasic trihydrate (≥99.0% purity) from Sigma-Aldrich (Steinheim, Germany), and sodium acetate trihydrate (≥99.5%) and potassium dihydrogen phosphate (≥99.5% purity) from Fluka Chemie GmbH. A basic 20+ pH meter from Crison (Alella, Spain) was used to measure the pH. A single-beam UV-visible spectrophotometer (UVmini-240, Shimadzu, Tokyo Japan), equipped with quartz cuvettes having a 1 cm optical path length was used to measure spectra. Ultra-pure water was prepared in an EASYpure RF water purification system (Barnstead/Thermolyne Corporation, Dubuque, IA, USA).

The natural samples used here were: (i) river water sampled from the river Koiliaris at Kyani Akti (Kalyves, Crete, Greece); (ii) seawater sampled near the beach of Koum Kapi in Chania, Crete, Greece, and (iii) rainwater collected at the campus of the Technical University of Crete in Chania. The compositions of the natural water samples are given in Table A1 in the Appendix. All samples were initially filtered, analyzed to ensure that they were free of nicotine, and then stored in the dark at 4 °C until use.

2.2. Tobacco products and their leachates

The HEETS Sienna Selection tobacco units were used to study HnBs and the Marlboro Red Label brand for studying CCs. Both tobacco products were purchased from the local distributor in Chania-Crete, Greece. Tobacco products were operated in a programmable single port machine-smoking from Burghart (Wedel, Germany) and the puffing parameters were set according to a published procedure (Koutela et al., 2020). For HnBs, the IQOS™ 2.4 Plus tobacco heating device (Philip Morris Products S.A., Neuchatel, Switzerland) was used for operation. The CCs were ignited using a flameless lighter and were smoked until a predefined butt length (length of the filter plus approximately 3 mm of

the tobacco plug).

For the preparation of leachates, tobacco products were submerged and allowed to soak in deionized water for 24 h at room temperature, unless otherwise stated in the text. Leaching proceeded in 40 mL clear glass vials equipped with caps. An approximate 10 L kg^{-1} liquid-to-solid ratio was used, which, depending on the experiment, corresponded to: 4 unused HnBs, 4 used HnBs or 4 unused CCs soaked in 31 mL water and 10 smoked CCs in 25 mL of the aqueous phase. Freshly made leachates were used for each experiment. Leachates were diluted using ultrapure water to a final 10 mg L^{-1} nicotine concentration and used for photolysis experiments.

The total organic carbon (TOC) content of leachates was measured on filtered suspensions using a TOC-5000 analyzer (Shimadzu, Kyoto, Japan; catalytic oxidation on Pt at 680°C). The calibration was performed using standards of potassium phthalate.

The determination of the total and bioavailable nicotine concentrations in unused and used tobacco products and their leachates was based on a standard procedure using solvent extraction followed by gas chromatography-flame ionization detection (GC-FID) (World Health Organization (WHO), 2014). The experimental procedure is discussed in details in Section S.1 in the Appendix.

2.3. Photolysis experiments

All UV₂₅₄ irradiation experiments were performed in a home-made laboratory photoreactor ($28 \text{ cm} \times 28 \text{ cm} \times 28 \text{ cm}$). The photoreactor was equipped with two 8 W low-pressure mercury lamps (Osram HNS 8 W G8T5) having a strong emission line at 254 nm and mounted on opposing sidewalls of the photoreactor and each one. The distance between each lamp and the quartz vial used in the experiments was set to 13 cm. The quartz vial was placed on top of a magnetic stirrer that was switched on during photolysis. In all photolysis experiments, 10 mL aqueous solution or leachate having a known nicotine concentration was placed in a tailor-made quartz vial (2.4 cm outer diameter \times 2.0 cm inner diameter \times 5.2 cm height) and submitted to UV irradiation for a preset time. The incident photon flux entering the solution (I_0 , given in $\text{E L}^{-1} \text{ s}^{-1}$, where E = Einstein) was determined using H_2O_2 as a chemical actinometer (Kourounioti et al., 2019), and was found equal to $I_0 = (6.11 \pm 0.22) \times 10^{-6} \text{ E L}^{-1} \text{ s}^{-1}$. All experiments were run in triplicates.

During the photolysis of nicotine containing ultrapure or natural water samples, 50 μL samples were removed at preset exposure times and used for liquid chromatography/mass spectrometry analysis (LC/MS). The remaining sample solution was UV-irradiated until complete conversion of nicotine. Tobacco product leachates could not be directly injected in an analytical instrumentation. The analytical procedure used for these samples included a sample preparation step that used HiSorb sorbent units for the extraction of nicotine followed by thermodesorption gas chromatography-ion trap mass spectrometry analysis (TD-GC/ITMS). The sample preparation procedure is discussed in details in Section 2.5 that follows. For tobacco product leachates, fresh solutions had to be irradiated for studying each exposure time, as, each time, 9 mL of the 10 mL irradiated solution had to be extracted and used for analysis.

For each set of experiments, dark tests were run in parallel by placing the samples inside the photoreactor with the lamps switched off. These tests confirmed that changes in the analytical signal were due to the action of photons alone.

2.4. LC/MS analytical procedure used for ultrapure and natural water spiked samples

All analyses of nicotine containing ultrapure or natural water samples were carried out using an Agilent 1200 Series high-performance liquid chromatography system equipped with a binary pump, autosampler, degasser and thermostated column compartment coupled to a diode array detector (DAD), and an Agilent 6110 single quadrupole LC/

MS system equipped with a multimode ionization source. For analysis, 50 μL of the irradiated sample were added in 250 μL glass inserts placed in 2 mL glass autosampler vials equipped with septum caps, all purchased from Agilent (Palo Alto, USA). The injection volume was 20 μL . A Thermo-Electron Betasil C18 column (Waltham, MA, USA) of dimensions $2.1 \text{ mm ID} \times 100 \text{ mm length}$ and $5 \mu\text{m}$ particle size was used for separation. The mobile phase consisted of solvent (A) ultrapure water containing 0.1% formic acid (v:v) and (B) acetonitrile containing 0.1% formic acid (v:v). The LC gradient method used was 2% B for the first 1 min, then linearly increased to 100% B in 10 min, held for 2 min, followed by a 0.5 min ramp to 2% B where it was held for the rest of the analysis. Column temperature was set to 30°C and the flow rate of the mobile phase was $300 \mu\text{L min}^{-1}$, while the total analysis time was 20 min. The MS conditions were: drying gas flow, 8 L min^{-1} ; drying gas temperature, 250°C ; nebulizer pressure, 30 psi; collector capillary voltage, 4.0 kV; fragmentor voltage, 70 V; scan range (m/z) of 100–1000 amu for signal 1 and the scan range 160–165 amu was used for nicotine. The mass spectrometry data were recorded using the positive electrospray ionization (ESI) mode.

2.5. TD-GC/ITMS analytical procedure used for tobacco product leachates

The analyses of tobacco product leachates included a sample preparation step, where 9 mL of the irradiated solution were placed in 10 mL vials and capped with a HiSorb cap and septum (Markes International). A HiSorb unit having a 63 μL polydimethylsiloxane (PDMS) coating (Markes International) was introduced through the septum and the PDMS coating was immersed into the leachate. Extraction occurred for 60 min at 40°C and 300 rpm using a HiSorb Agitator from Markes International. Once extraction was completed, the HiSorb unit was removed, washed to remove residual matrix, dried with a lint-free tissue, and inserted in a stainless-steel thermal desorption tube (Markes International) for analysis using TD-GC/ITMS.

The analytical instrumentation used for these analyses was a Varian 450-GC coupled with a Varian 240-MS ITMS (Varian, Walnut Creek, CA, U.S.A.) and fitted with a TD100-xr™ (Markes International). HiSorb units were thermally desorbed at 250°C for 5 min with a trap flow of 50 mL min^{-1} . Following desorption, the sample was collected on a 'General Purpose' cold trap at 30°C . The cold trap was purged for 1 min at 50 mL min^{-1} and was sequentially desorbed for 3 min at 320°C with a split flow of 10 mL min^{-1} . The flow path temperature was set at 150°C . Separation of desorbed analytes proceeded on a MEGA-5 HT capillary column ($30 \text{ m} \times 0.25 \text{ mm i.d.}$, $0.25 \mu\text{m}$ film thickness; MEGA S.r.l., Legnano, Italy). The column was held at 50°C for 5 min, increased to 160°C at $10^\circ\text{C min}^{-1}$ rate, held for 2 min, and again ramped to 310°C at a rate of 5°C min^{-1} where it was held for 5 min. Helium ($>99.99\%$ pure) was used as a carrier gas at 1.1 mL min^{-1} flow-rate. Manifold, ion trap, ion source and transfer line temperatures were maintained at 45, 180, 200 and 220°C , respectively. The detection and quantification of nicotine proceeded using selected ion storage at $m/z = 161$.

The above analytical procedure was also used to monitor the formation of by-products during the photolysis of 10 mg L^{-1} nicotine ultrapure water solutions. In this case, irradiated samples were extracted according to the procedure described above, the only difference being that the MS was set in the full scan mode from 50 to 500 m/z.

3. Results and discussion

3.1. Effect of concentration on the direct photolysis of nicotine

A past report studying the elution of nicotine from average cigarette butts in a simulated rainfall experiment, estimated nicotine concentrations in the run-off water to reach 0.62 mg L^{-1} with local concentrations as high as 11.4 mg L^{-1} (Roder Green et al., 2014). In the same report, batch experiments were also run representing the elution dynamic when

cigarette butts come into contact with standing water, such as a lake or a river, but also puddles in street or sidewalk depressions caused by precipitation. The authors concluded that the total releasable nicotine concentration from CCs was released after 24 h of cigarette exposure to water, and was measured 7.1 mg g^{-1} , which is equivalent to 2.13 mg L^{-1} according to the experimental conditions set (Roder Green et al., 2014).

A series of photodegradation experiments were carried out for initial nicotine concentration varying from 1 to 20 mg L^{-1} , and the resulting concentration time profiles are given in Fig. 1. In all cases, the direct photolysis of nicotine was recorded until complete conversion, reflecting the good overlap between the 254 nm emission peak of the low-pressure mercury lamps used here and the maximum absorption band of nicotine ($\sim 261 \text{ nm}$). To quantify degradation rates, a pseudo-first order kinetic expression with respect to nicotine concentration was considered by applying equation (OECD, 2008)

$$[NIC]_t = [NIC]_0 e^{-k_{NIC} t} \quad (1)$$

where $[NIC]_0$ is the initial concentration of nicotine, $[NIC]_t$ is the concentration of nicotine at time t , and k_{NIC} is the pseudo first-order reaction rate. The inset graph (i) in Fig. 1 depicts the computed rate constants k_{NIC} , which took values of 0.50 ($r^2 = 0.9991$), 0.18 ($r^2 = 0.9999$), 0.10 ($r^2 = 0.9949$) and 0.05 min^{-1} ($r^2 = 0.9896$) at respectively, 1, 5, 10 and 20 mg L^{-1} $[NIC]_0$. As seen, k_{NIC} decreased with increasing initial nicotine concentration, implying that the reaction kinetics did not follow a true first order (where the rate constant is independent of the nicotine concentration), and shifted towards zeroth order at higher $[NIC]_0$ due to absorption saturation (Kourouniotti et al., 2019). The initial nicotine photodegradation rates (R_{NIC}^0) were then calculated using the simple pseudo-first order approximation $R_{NIC}^0 = k_{NIC} [NIC]_0$ (Braslavsky, 2007). The resulting R_{NIC}^0 vs $[NIC]_0$ profile (inset graph (ii) in Fig. 1) showed an increase followed by a plateau. The cause of this plateau trend in direct photolysis is usually absorption saturation, confirming that nicotine absorbed radiation and became photolyzed up to saturation (Kourouniotti et al., 2019).

In general, the photolytical degradation mechanism of nicotine is a complex process and past reports investigated the reactions involved during indirect photolysis of the parent compound (Lian et al., 2017; Medana et al., 2016; Passananti et al., 2014). Here, exposing aqueous solutions of nicotine to UV_{254} irradiation afforded the photo-transformation of the parent compound to different photoproducts. The amount of organics remaining in the system after treatment was evaluated by measuring the TOC of a 10 mg L^{-1} nicotine solution before and after 30 min of UV_{254} exposure. Although nicotine removal

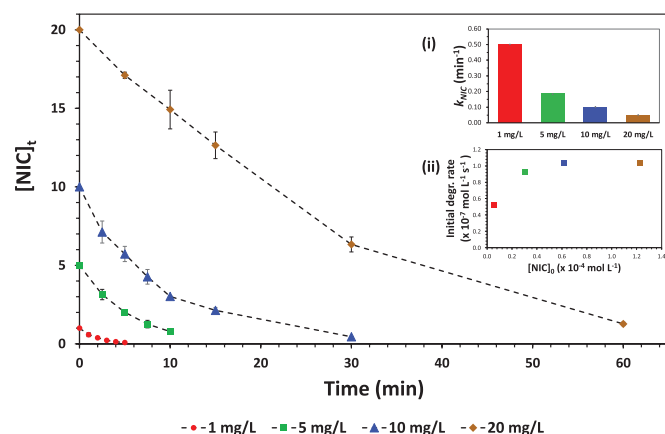


Fig. 1. Effect of concentration on the UV_{254} -induced photolysis of nicotine in ultrapure water. Inset graphs: (i) apparent rate constants for each concentration tested and (ii) initial nicotine degradation rates as a function of concentration. Data points are linked with dashed lines to visualize trends. Some error bars are too small to be visible.

was almost complete after this irradiation time, only a 9.5% TOC removal was recorded. This observation pointed towards the formation of degradation products at different rates during irradiation that were more recalcitrant than the parent compound. Indeed, several photo-products eluted during LC/MS analysis, but not all of them could be identified either because they consisted of isomers or because they co-eluted with other by-products. To increase the number of identified photo-products, irradiated samples were also analyzed using the TD-GC/ITMS analytical procedure. The summary of these investigations is given in Table A2 in the Appendix. During TD-GC/ITMS analysis, the formation of 3-ethenylpyridine (P105 in Fig. 2) was confirmed at $m/z = 105$ and the MS spectrum had an excellent match with the MS library. The formation of P105 has been reported in the past during the photocatalytic degradation of cotinine at $\lambda = 360 \text{ nm}$ in the presence of TiO_2 (Medana et al., 2016). Cotinine is an important product of nicotine during ozonation, $OH\cdot$ oxidation, biodegradation, and during the indirect photolysis of nicotine in wastewater samples (Lian et al., 2017; Medana et al., 2016). It was therefore assumed that during direct photolysis, nicotine was oxidized to cotinine and further photo-transformed to P105. Here, the presence of cotinine (Fig. 2) was confirmed during LC/MS at $[M-H]^+ = 177 \text{ m/z}$. Other transformation by-products identified during LC/MS included P135, P181 and P208 at $[M-H]^+ = 136, 182$ and 209 m/z respectively. The formation of these by-products has been proposed in the past during the indirect photolysis of nicotine together with their reaction pathways (Lian et al., 2017).

3.2. Effect of pH on the direct photolysis of nicotine

In general, the relationship between photolysis and pH is linked to the protonation states of the molecule and the absorption spectrum of the substrate (Boreen et al., 2004). Once dissolved in water, nicotine may be present in a neutral or ionic form, depending on the pH of the water solution. Fully protonated nicotine carries two protons and the reported acidity constants in water are $pK_{a1} = 3.37$ and $pK_{a2} = 8.07$ at 25°C (Nienow et al., 2009). At pH values below 4.0 the diprotonated nicotine is the principal species, between pH values 4–8 monoprotonated nicotine is dominant, and at higher pH values the neutral form of nicotine is dominant (Nienow et al., 2009).

To investigate the effect of pH at environmentally relevant values, nicotine containing water solutions having pH values between 5 and 9 were UV_{254} irradiated. All irradiated water solutions were buffered and the pH was monitored before and after photolysis to confirm that there were no changes in the pH. Fig. 3 depicts the time trends in normalized nicotine concentration during irradiation at the pH values tested. As seen, at pH 4.9 and 6.9 (where the monoprotonated form of nicotine is the primary species present) decomposition was faster compared to that at pH 9.0. The apparent pseudo-first order rate constants (k_{NIC} was 0.16 min^{-1} ($r^2 = 0.9937$), 0.12 min^{-1} ($r^2 = 0.9837$) and 0.04 min^{-1} ($r^2 = 0.9996$) at pH 4.9, 6.9 and 9.0 respectively) confirmed the enhanced photodegradation rate of nicotine when the monoprotonated nicotine species is the most abundant. The present results were in agreement with some preliminary experiments performed whilst investigating the H_2O_2 -enhanced photodegradation of nicotine (Nienow et al., 2009). In this report, UV_{254} irradiation of nicotine water solutions at pH = 1, 5.5, and 11.3 provided evidence that the direct photolysis of nicotine is faster when the monoprotonated nicotine is the primary species present in solution.

3.3. Effect of dissolved species on the direct photolysis of nicotine

Humic acids (HA) have a considerable light absorbing capacity and can act as photosensitizers by generating a range of reactive transient species (Kourouniotti et al., 2019; Koutantou et al., 2013). During the present investigations, the presence of HA at an environmentally relevant concentration (2.5 mg L^{-1}), had a very small effect on the direct photolysis of a 10 mg L^{-1} nicotine water solution (Fig. A1 in the Appendix) yielding $k_{NIC,HA} = 0.08 \text{ min}^{-1}$ ($r^2 = 0.903$). It was assumed that this

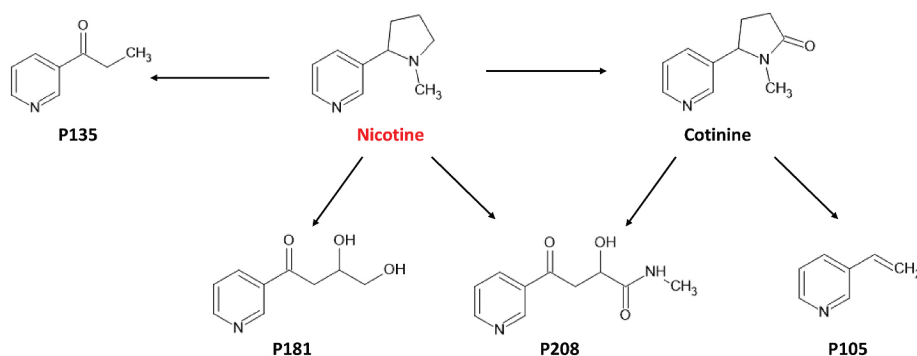


Fig. 2. Identified photoproducts during the direct photolysis of nicotine.

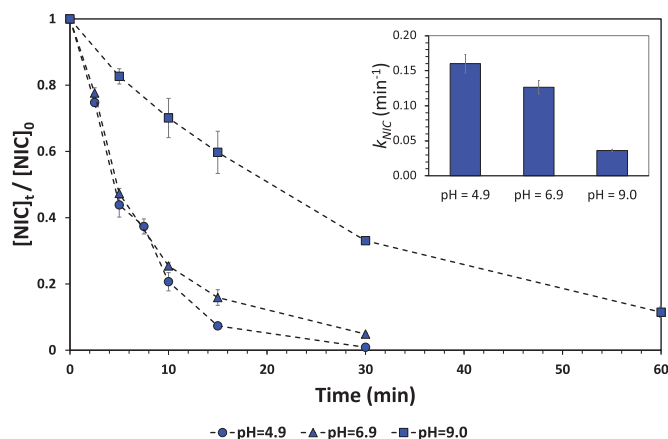


Fig. 3. The effect of pH on the direct photolysis of 10 mg L⁻¹ nicotine solutions under UV₂₅₄ irradiation. Inset graph: apparent rate constants for each pH tested. Data points are linked with dashed lines to visualize trends. Some error bars are too small to be visible.

small delay in kinetics was due to competition for lamp irradiance between nicotine and HA (Kourouniotti et al., 2019). In further experiments, the effect of salt was also investigated and the results from these studies are shown in Fig. A1 in the Appendix. In general, salt can alter the ionic strength of the solution and lower the activity coefficient of the mono-protonated and especially the di-protonated species (Nienow et al., 2009; Schwarzenbach et al., 2003). The negatively charged chloride ions may thus result in a shielding effect of the positively charged nicotine ions, which in turn may decrease observed reaction rates of nicotine when free radicals are involved (Nienow et al., 2009). During the present investigations and as expected, the presence of 3.5% w:v NaCl had practically no effect on the direct photolysis of 10 mg L⁻¹ nicotine water solutions ($k_{\text{NIC, NaCl}} = 0.11$ ($r^2 = 0.9871$)).

3.4. The photodegradation of nicotine in natural waters

The photodegradation of nicotine was also studied in various natural water matrices (rain, river and sea water), and compared to the behavior of nicotine in ultrapure water (Fig. 4). In the case of sea water, the kinetics of nicotine photolysis were practically the same as in ultrapure water ($k_{\text{NIC, sea}} = 0.10$ ($r^2 = 0.9833$)) and for this matrix type, the natural-water components could not alter the photolysis kinetics of nicotine. This conclusion was also supported by the no-effect of salt found earlier on the direct photolysis of nicotine. On the other hand the degradation of nicotine was slightly delayed in river water ($k_{\text{NIC, river}} = 0.08$ ($r^2 = 0.9880$)). It was assumed that this was the result of light-absorbing components present in this type of surface water that

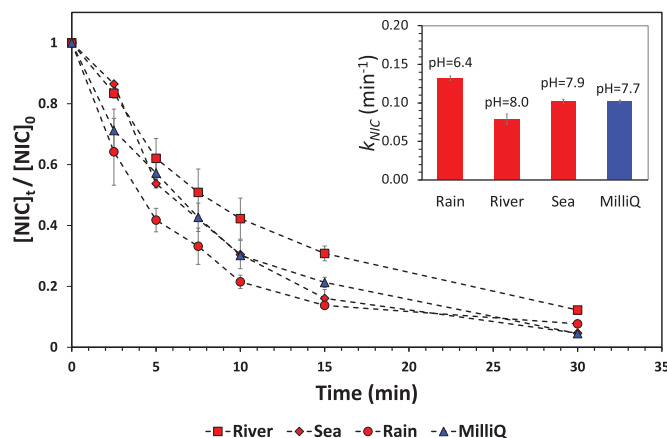


Fig. 4. Photolysis of 10 mg L⁻¹ nicotine solutions in rain, river and sea water under UV₂₅₄ irradiation. Inset graph: apparent rate constants for each natural water tested. The results in non-buffered ultrapure (MilliQ) water are also included. Data points are linked with dashed lines to visualize trends. Some error bars are too small to be visible.

competed with nicotine for lamp irradiance and reduced the photon flux absorbed by nicotine, in agreement with our previous results on the effect of HA on the direct photolysis of nicotine. Finally, the direct photolysis kinetics of nicotine in rain water (Fig. 4) appeared to be somewhat enhanced compared to the rest of the natural water samples tested ($k_{\text{NIC, rain}} = 0.13$ ($r^2 = 0.9871$)). This observation was assumed to be the result of the pH of this matrix. Indeed, compared to the rest of the natural water samples tested, rain water sample was more acidic (pH = 6.4; pH values given in the inset of Fig. 4), and kinetics were closer to the one recorded for ultrapure water at pH = 6.9 where $k_{\text{NIC}} = 0.12$.

3.5. Nicotine photolysis in leachates produced from used tobacco products

3.5.1. Preliminary studies on the leaching behavior of nicotine from HnBs and CCs

Tobacco consists of a very complex mixture having at least 4000 chemical constituents (Slaughter et al., 2011). Moreover, in a burning cigarette or a heated HnB many chemical reactions take place, that yield a number of new compounds (Baker and Bishop, 2004; Schaller et al., 2016). The leachates from tobacco product waste therefore consist of highly complex mixtures of compounds. In a preliminary set of experiments, leaching studies were performed using batch tests with unused or used HnBs and CCs soaked in ultrapure water for times ranging between 30 min to a maximum of 30 days, and the changes in TOC values were monitored. For each tobacco product, the results showed slower kinetics of organic content release from unused compared to operated units

(Fig. A2 in the Appendix). Moreover, a slower release was observed in leachates from HnBs compared to CCs regardless whether the product was operated or not (Fig. A2 in the Appendix). This observation presumably reflected the differences in tobacco processing between the two products as well as the presence of a thin aluminum sheet to wrap the tobacco plug in HnBs, which also delayed the disintegration of tobacco sticks in water. In all cases, the TOC values after 24 h of leaching remained unchanged as the system was at equilibrium.

In tobacco product leachates, nicotine accounts only for a small amount of the carbon-containing compounds. Here, the nicotine contribution to the TOC values of leachates was $\sim 5\%$ for unused and operated HnBs, and 9% for unused and smoked CCs. Nonetheless, nicotine is a highly water-soluble compound, assumed to be released quickly to the water phase from tobacco products and become bioavailable to aquatic life (Roder Green et al., 2014). The total and bioavailable nicotine concentrations were then measured for HnBs and CCs before and after being operated, since not all of these values are reported in the literature. For HnBs, the total nicotine content was $4.67 \pm 0.09 \text{ mg unit}^{-1}$ (past reported value was 4.7 mg unit^{-1} (Bekki et al., 2017)), and after operation the total nicotine content was reduced to $3.20 \pm 0.09 \text{ mg unit}^{-1}$ (Table A3 in the Appendix). For CCs the total nicotine content was $9.46 \pm 0.34 \text{ mg unit}^{-1}$ (past reported value was $10.9 \text{ mg unit}^{-1}$; differences were accounted to tobacco variations in different countries and among CC packs (Kozłowski et al., 1998)), and after smoking CCs, this value was reduced to $1.55 \pm 0.11 \text{ mg unit}^{-1}$ (Table A3). Moreover, for all types of tobacco product tested, the majority of the total nicotine content was bioavailable after 24 h (Table A3). These results showed that $\sim 70\%$ of the total and bioavailable nicotine content remained in the HnBs units after operation and that this percentage dropped to $\sim 15\%$ for CCs (Table A3). This drastic decrease in nicotine content for CCs was accounted to the reduction in length and mass after smoking (Koutela et al., 2020). This assumption was further supported by the similar TOC values in leachates from used CCs and unused CCs cut at an operated length i.e. length of the filter plus 3 mm of the tobacco plug (Fig. A2 in the Appendix). Further studies on the contribution of the different parts of the tobacco product (filter, tobacco filler and paper) on the total and bioavailable nicotine content of HnBs and CCs showed that tobacco was the only source of nicotine from both types of unused tobacco products (Table A3 in the Appendix). However, after operation, nicotine was evenly distributed in the remnant tobacco and filter and to a less extent in the paper used for tobacco wrapping (Table A3). We also found that the bioavailable nicotine concentrations remained practically the same when varying the pH, salt and humic acid content at environmentally relevant values (Table A4 in the Appendix) and when river water, rain water or seawater was used as leachant (Table A5 in the Appendix).

3.5.2. Nicotine photolysis in leachates produced from used tobacco products

Leachates were prepared from used HnBs and smoked CCs at a 10 L g^{-1} liquid-to-solid ratio and further diluted to a 10 mg L^{-1} initial nicotine concentration (pH ~ 6.5 for the diluted solutions). Aliquots were then UV₂₅₄ irradiated and the resulting normalized concentration-time profiles are given in Fig. 5. Despite the complexity of the matrix, the respective coefficients of linear regression after data fitting to Equation (1) were satisfactory and the resulting pseudo first-order reaction rates were: $k_{\text{NIC,CC}} = 0.11$ ($r^2 = 0.9812$) and $k_{\text{NIC,HnB}} = 0.09$ ($r^2 = 0.9947$). As seen, nicotine degradation in these leachates proceeded possibly in slightly slower kinetics compared to ultrapure water (at pH = 6.9 $k_{\text{NIC}} = 0.12$ ($r^2 = 0.9837$)). This was somewhat expected considering the increased complexity of the leachate compared to ultrapure water where nicotine accounted only for a small amount of the carbon-containing compounds. It was therefore assumed that the presence of other tobacco-derived leachate components absorbed UV₂₅₄ light and decreased the irradiance available for the direct photolysis of nicotine (Kourounioti et al., 2019).

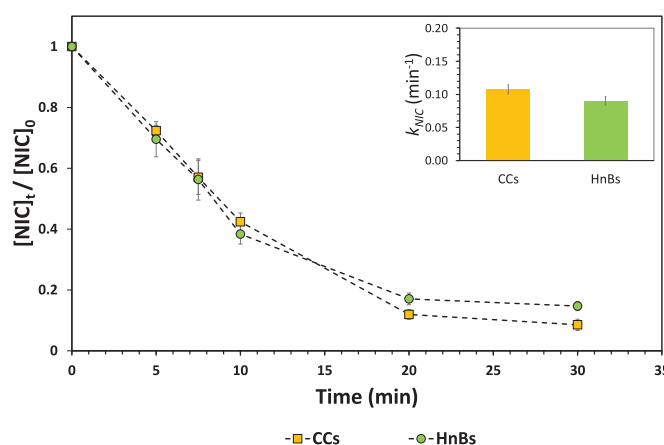


Fig. 5. UV₂₅₄-induced photolysis of nicotine in leachates from used HnBs and CCs. Inset graph: apparent rate constants for each tobacco product leachate tested. Leachates were diluted to a $[\text{NIC}]_0 = 10 \text{ mg L}^{-1}$. Data points are linked with dashed lines to visualize trends.

Identification of the photo-transformation products formed under UV₂₅₄ irradiation was not possible due to the large number of co-eluting extracted organics that impeded untargeted analysis when using one-dimensional GC and the current type of mass spectrometry. To allow a better understanding of leachates, the organics remaining in the system after irradiation were evaluated in terms of TOC. The measured changes in TOC values after irradiation were non-significant even after extending the exposure time to 180 min. It was concluded that despite the complete conversion of nicotine under UV₂₅₄, the mineralization degree of leachates in terms of TOC values was negligible due to the abundance of organics and the formation of new transformation products.

4. Concluding remarks

In this study, we report the direct photolytical degradation of nicotine in simple and highly complex matrices. The results showed that UV₂₅₄-induced photolysis is an efficient and fast process for the degradation of nicotine. Among the different photoproducts formed, only five were identified by means of LC/MS and TD-GC/ITMS. TOC removal was very low pointing towards the formation of photoproducts at different rates that were more recalcitrant than the parent compound. The photodegradation kinetics was found dependent on the pH and optimum conditions were found in the range where monoprotonated nicotine prevails. Humic acids slightly delay kinetics by screening light, whereas the presence of salt did not affect the reaction. From all the natural water tested, faster kinetics were recorded in rain water due to the lower pH value of this matrix. Leachates from operated CCs and the new generation HnBs were UV₂₅₄ irradiated and photolysis proceeded fast despite the large amount of tobacco-derived components present in the solution. Nonetheless, TOC removal from both leachates was non-significant.

More information is needed to elucidate the photochemical fate of nicotine. The use of two-dimensional gas chromatography (GC \times GC) will allow enhanced separations of the complex leachate mixtures through greater chromatographic peak capacity that will enable the identification to the maximum possible extent of the photoproducts formed in highly complex matrices like tobacco product leachates.

Finally, we take advantage of the present investigations and perform for the first time leaching studies on unused and operated HnBs and CCs. Slower kinetics of organic content release were recorded for HnBs products. After operation, $\sim 70\%$ of the total and bioavailable nicotine content remains in HnBs compared to the 15% in CCs. This finding confirms the importance of properly disposing tobacco product waste to prevent nicotine leaching in water bodies.

Author statement

Stefano Alberti: Investigation, Visualization, Writing – original draft. Maria Sotiropoulou: Investigation. Elena Fernández: Investigation, Visualization, Validation, Nicoleta Solomou: Formal analysis. Maurizio Ferretti: Writing – review & editing. Eleftheria Psillakis: Conceptualization, Funding acquisition, Supervision, Visualization, Writing – review & editing

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2020.110695>.

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