Direct photolysis of polycyclic aromatic hydrocarbons in drinking water sources

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ARTICLE INFO

ABSTRACT

The widely used low pressure lamps were tested in terms of their efficiency to degrade polycyclic aromatic hydrocarbons listed as priority pollutants by the European Water Framework Directive and the U.S. Environmental Protection Agency, in water matrices with very different compositions (laboratory grade water, groundwater, and surface water). Using a UV fluence of 1500 mJ/cm², anthracene and benzo(a)pyrene were efficiently degraded, with much higher percent removals obtained when present in groundwater (83–93%) compared to surface water (36–48%). The removal percentages obtained for fluoranthene were lower and ranged from 13 to 54% in the different water matrices tested. Several parameters that influence the direct photolysis of polycyclic aromatic hydrocarbons were determined and their photolysis by-products were identified by mass spectrometry. The formation of photolysis by-products was found to be highly dependent on the source waters tested.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) occur widely in the environment, being introduced by natural and anthropogenic activities such as forest fires, volcanic eruptions, incomplete combustion of organic materials (coal, fossil fuels, and wood), incineration of industrial and domestic wastes, transportation, and other industrial processes [1]. These micropollutants are very difficult to degrade due to the high stability and complexity of the PAHs' molecular structures [2]. PAHs are non polar and very hydrophobic compounds with low water solubility. Therefore, in the aquatic environment they are commonly found adsorbed on the suspended and particulate matter, as well as in sediments [3], but their occurrence have also been reported in concentrations ranging from 1 ng/L to 72.4 µg/L in groundwater and surface water matrices [4,5]. PAHs are well known environmental persistent pollutants with toxic, carcinogenic, and mutagenic properties. Many of these compounds are therefore listed as priority pollutants by the European Union [6] and the U.S. Environmental Protection Agency [7].

Conventional surface water treatment often includes coagulation, flocculation, sedimentation, filtration, and final disinfection. Final disinfection using chlorine is widely used and guarantees a residual protection in the distribution system. However, chlorine reacts with the natural organic matter present in the water and produces disinfection by-products which have been linked to different types of cancers and adverse reproductive outcomes [8,9]. The use of low pressure (LP) ultraviolet (UV) photolysis for water disinfection has been widely described due to its efficiency and the consequent reduction of the chlorine dose needed to achieve disinfection in water treatment facilities [10]. In addition, it has also been described to be very effective in achieving the degradation of a wide range of photolabile organic micropollutants using higher UV fluences [11–14].

Different UV sources have been used to study the photolysis of PAHs such as low pressure lamps [15–18], medium pressure lamps [15,17–19], UV lamps that emit mainly radiation at 365 nm [20,21], higher than 290 nm [22], and Xe arc lamps simulating sunlight [23]. The efficiency of the different UV lamps to degrade PAHs depends on the target PAH and its capability to absorb radiation at certain wavelengths. For instance, Miller and Olejnik [15] observed that medium pressure UV lamps are more efficient than low pressure lamps for the photolysis of benzo(a)pyrene but the opposite was obtained for chrysene and fluorene using the same system. Therefore, the structure and properties of PAHs have an important role in their photodegradation since PAHs with higher molecular weight,

molecular polarizability, and heat of formation often have lower photolysis quantum yields [24,25].

Few studies have addressed the efficiency of LP/UV photolysis to degrade PAHs such as anthracene, fluoranthene, and benzo(a)pyrene [15,16], which are included in the list of priority substances mentioned above. Miller and Olejnik [15] reported a fast degradation of benzo(a)pyrene spiked in a mixture of laboratory grade water and methanol using LP/UV lamps under different experimental conditions. Another study [16] reported a more rapid degradation of anthracene and benz(a)anthracene than pyrene and dibenz[a,h]anthracene using LP direct photolysis in laboratory grade water.

The composition of the water has been found to impact the photodegradation of PAHs [22,23,26]. The concentration of organic matter in water influences the photodegradation of PAHs in two different ways: accelerating the degradation by stimulating the production of the highly reactive hydroxyl radical or inhibiting the degradation due to the competition of the matrix components for the absorption of radiation [22,23]. In addition, organic matter was even found to impact differently the photodegradation of different PAHs. Xia et al. [23] reported that fluoranthene photodegradation was accelerated with the decrease of the matrix fulvic acids concentration, but this effect was not observed for all the tested PAHs. The ionic composition of the water also impacts the degradation of organic compounds, in particular due to the presence of the following ions: chloride, bromide, iron, and nitrate [26–28]. The presence of nitrate in the water has been reported to influence the degradation of different organic compounds by increasing their photodegradation rates due to its ability to form hydroxyl radicals [26,29,30]. Chloride ions were found to accelerate the photodegradation rates of phenicols using UV–vis radiation due to the formation of singlet oxygen [27]. However, studies conducted in different matrices and using different light sources may show contradictory effects in terms of the influence of nitrate and chloride in the degradation efficiency [e.g. 26–28].

Studies addressing the efficiency of photolysis to degrade PAHs have been mainly conducted in laboratory grade water [16,20,21], synthetic water matrices spiked with natural organic matter [22], and mixtures of water and organic solvents such as alcohol and methanol [15,19]. Very few studies were conducted to date that addressed the effect of natural water matrices composition such as groundwater and surface water on the degradation of PAHs [18,22]. Fasnacht and Blough [22] addressed the influence of a synthetic water spiked with 5 mg/L of natural organic matter and three surface waters in the degradation of anthracene, fluoranthene, and benzo(a)pyrene using UV lamps that emit radiation higher than 290 nm. In that study, the photolysis of anthracene was enhanced when the compounds were spiked in different natural water sources and the synthetic water matrix comparatively to laboratory grade water while benzo(a)pyrene degradation decreased in the different surface water matrices. The degradation of fluoranthene was also increased in the natural water matrix. Further studies should be conducted to address the photolysis efficiency of different UV sources and the effect of natural water matrices with very different compositions to provide a better insight on the degradation behavior of priority PAHs in water treatment facilities. Besides the decrease in the concentration of organic compounds, the overall efficiency of UV photolysis should also be evaluated taking into consideration the possible formation of photolysis by-products that may be even more toxic and persistent than the parent compounds [20,31,32]. Woo et al. [20] reported the identification of the by-products formed during the degradation of anthracene using lamps that emit mainly radiation at 365 nm. However, even though general pathways for the photodegradation of PAHs have been proposed [15,22], the reaction by-products formed

may be different according to the photolysis system and experimental conditions.

LP/UV lamps are the most widely used in drinking water facilities. This study reports the efficiency of LP/UV photolysis to remove three PAH compounds (anthracene, fluoranthene, and benzo(a)pyrene) considered as priority by the European Water Framework Directive [6] and the U.S. Environmental Protection Agency [7]. These three PAH compounds were selected due to their different structures in terms of the number of aromatic rings and consequent different chemical properties and reported toxicities [7]. From the three target PAHs, benzo(a)pyrene is the most toxic compound, being classified as a probable human carcinogen by the U.S. Environmental Protection Agency [7].

The compounds were spiked in laboratory grade water and natural water matrices with very different compositions – groundwater and surface water. The by-products formed during the photolysis experiments conducted in different water matrices were identified by mass spectrometry and a degradation pathway was proposed.

2. Experimental

2.1. Reagents

All polycyclic aromatic hydrocarbons were purchased as solids or solutions of the highest grade commercially available, ≥98.9% (Sigma–Aldrich, Germany). HPLC grade acetonitrile from Lab Scan Analytical Sciences (Poland) was used for the chromatographic analysis of the PAHs and preparation of stock solutions. The Milli-Q water used in the photolysis experiments and in the chromatographic analysis was produced by a Milli-Q water system (Millipore, CA, USA). The natural water matrices (groundwater and surface water) were collected in brown glass bottles, filtered through 0.45 μm mixed esters of cellulose filters (Millipore, CA, USA) and stored at 4 °C until used.

2.2. UV photolysis experiments

UV photolysis experiments were conducted in a collimated beam bench-scale reactor (Trojan Technologies Inc., Canada), equipped with a mercury low pressure UV lamp that emits primarily monochromatic light at 254 nm. Concentrated PAH stock solutions were prepared in acetonitrile, individually spiked in 100 mL of laboratory grade water and real water matrices to achieve a concentration of 3.9–5.6 μM, and thoroughly mixed. 50 mL of the solution were placed in a Petri dish beneath the UV source and were continuously stirred during the photolysis experiments while the remaining 50 mL were used as control to account for possible losses of the PAHs due to degradation, evaporation, and adsorption to the Petri dish walls. The control samples were continuously stirred and kept in the dark under similar experimental conditions as the irradiated solution. Noticeable differences in the concentration of the controls were not detected. The photolysis experiments were conducted at room temperature (21 ± 2 °C).

Samples were taken at different UV fluences (approximately 0, 40, 100, 500, 750, 1000, and 1500 mJ/cm^2) that correspond to different exposure times, which were determined taking into account the lamp irradiance and many parameters that affect photolysis such as the Petri, reflection, water, and divergence factors [33]. The lamp irradiance was measured using a calibrated radiometer (IL1700, International Light, Newburyport, MA) which was placed at the same height of the water level in the Petri dish, and the solution transmittance was measured by a UV photometer (P254C, Trojan Technologies Inc.). At the defined UV fluences, 200 μL of the photolysis and control samples were taken and analyzed by direct

Table 1
Characterization of the water matrices used in the LP/UV photolysis experiments.

Parameter	Surface water	Groundwater	Laboratory grade water
Temperature ($^\circ$C)	22.4	20.8	25.5
pH	7.90 ± 0.26	7.42 ± 0.24	6.13
Total organic carbon (mg/L, C)	3.56 ± 0.36	<0.4	<0.4
Turbidity (NTU)	12.5 ± 1.0	$<0.400 \pm 0.032$	<0.4
Alkalinity (mg/L, CaCO$_3$)	87.8 ± 7.0	233 ± 19	na
Total hardness (mg/L, CaCO$_3$)	209	274	na
Conductivity (μS/cm)	715	526	<18.2
Nitrates (mg/L, NO$_3$)	2.93 ± 0.35	3.21 ± 0.15	na
Chloride (mg/L, Cl)	91.3 ± 7.3	34.2 ± 1.8	na

na – not available.

injection using high pressure liquid chromatography (HPLC) with ultraviolet (UV) and fluorescence detectors (FLD).

2.3. Analytical methods

Both natural water sources selected (groundwater and surface water) were characterized in terms of temperature, pH, total organic carbon, turbidity, alkalinity, and total hardness. Temperature was determined by thermometry [34], pH by an electrometric method [35], total organic carbon by persulfate-ultraviolet oxidation [36], turbidity by a nephelometric method [37], alkalinity by a titration method [38], total hardness by a calculation method [39], conductivity by conductimetry [40], nitrate concentration by molecular absorption spectrometry, and chloride concentration by ionic chromatography.

The selected PAHs were analyzed by HPLC using a Waters system equipped with ultraviolet and fluorescence detectors (Waters Chromatography, Milford, MA, USA). A HyperClone 5 μm PAH (250 mm × 4.6 mm) column (Phenomenex Inc., Torrance, CA, USA) was used for the detection of the PAHs. Isocratic conditions with the following mobile phase compositions were used: 80% acetonitrile/20% water for the analysis of anthracene and fluoranthene and 100% acetonitrile for the detection of benzo(a)pyrene. The mobile phase flow rate used for the detection of anthracene was 1.5 mL/min while 1.2 mL/min was used in the detection of fluoranthene and benzo(a)pyrene. The oven temperature was set at 40 $^\circ$C for all the PAHs analysis. All the PAHs were monitored by UV and FLD. The same UV absorbance wavelength (λ), 210 nm, was used for the detection of all the selected PAHs while specific emission (em) and excitation (ex) wavelengths were used in the fluorescence detection: $\lambda_{em} = 400$ nm and $\lambda_{ex} = 250$ nm for anthracene; $\lambda_{em} = 450$ nm and $\lambda_{ex} = 280$ nm for fluoranthene; as well as $\lambda_{em} = 420$ nm and $\lambda_{ex} = 290$ nm for benzo(a)pyrene.

By-products formed during the UV photolysis experiments were identified by gas chromatography (GC) with mass spectrometry (MS) detection after sample concentration by liquid–liquid extraction (LLE).

In the liquid–liquid extraction procedure, dichloromethane (30 mL) was added to 50 mL sample and mechanical stirring was provided, after which the sample rested during 10 min. Then, the organic extract passed through a funnel with sodium sulphate anhydride and was collected into a concentration tube. This extraction step was repeated another two times, and the final extract was concentrated to a volume of 0.5 mL using a Turbovap evaporation system (Zymark, USA) with a nitrogen stream at 0.2 bar and at a temperature of approximately 35 $^\circ$C. 4 mL of dichloromethane were added to the extract that was then evaporated until 0.5 mL was achieved. The extract was finally analyzed by GC/MS.

Chromatographic analyses were carried out in a ThermoQuest Trace GC, equipped with an automatic injector, connected to a single quadrupole mass detector (Finnigan Trace, MS, USA). The chromatographic separation was performed with a HP-5MS (60 m × 0.25 mm × 0.25 μm) column from Agilent (USA). One microlitre of standard/organic extract was injected using the splitless mode and an injector temperature of 250 $^\circ$C. High-purity helium (99.9999%) was used as a carrier gas at a flow rate of 1.0 mL/min. Samples were analyzed using the following oven temperature programme: initial temperature 35 $^\circ$C (held for 1 min), increased by 50 $^\circ$C min^{-1} to 170 $^\circ$C (held for 1 min), increased by 1 $^\circ$C min^{-1} to 190 $^\circ$C, and finally increased by 50 $^\circ$C min^{-1} to 250 $^\circ$C (held for 20 min). MS detection was operated with electron impact (EI) mode; the ionization energy was set at 70 eV. The MS source and interface temperatures were 220 and 250 $^\circ$C, respectively. Full scan MS data were acquired over the range m/z 45–500 to obtain the fragmentation spectra of the analytes.

3. Results and discussion

Natural water sources – groundwater and surface water – with very different compositions in terms of organic and inorganic content were selected to address the effect of the water matrices in the degradation behavior of the selected priority PAHs – anthracene, fluoranthene, and benzo(a)pyrene. The characterization of the water matrices used is given in Table 1.

In terms of the real water matrices tested, Table 1 shows that the surface water matrix presents higher levels of total organic carbon and turbidity, while the groundwater samples contain higher alkalinity and total hardness.

Fig. 1 presents the experimental results obtained after direct photolysis of the selected PAHs in laboratory grade water and the natural water matrices.

The time-based pseudo-first order rate constants (k_t) for the direct photolysis of the individual PAHs were obtained from the slope of the linear regression described by Eq. (1).

$$-\frac{d[PAH]}{dt} = k_t[PAH] \Rightarrow \int_{PAH_0}^{PAH} \frac{1}{x}dx$$
$$= -k_t \int_{t_0}^{t} ds \Rightarrow \ln\frac{[PAH]}{[PAH_0]} = -k_t \times t \qquad (1)$$

where $[PAH_0]$ is the initial concentration of the PAHs (that ranged approximately from 3.9 to 5.6 μM) and $[PAH]$ is the concentration of the PAHs at a given time.

There are two parameters – decadic molar absorption coefficient (ε) and quantum yield (ϕ) – that highly impact direct photolysis kinetics [41]. The decadic molar absorption coefficient represents the probability of an organic compound to absorb UV light at a given wavelength [41] and was determined using Eq. (2).

$$a_{254nm} = \varepsilon_{254nm} \times [PAH] \times z \qquad (2)$$

where a_{254nm} is the solution absorbance measured at 254 nm, ε_{254nm} is the decadic molar absorption coefficient at 254 nm, and z is the cuvette path length (1 cm). The quantum yield can be defined

(a) Anthracene

(b) Fluoranthene
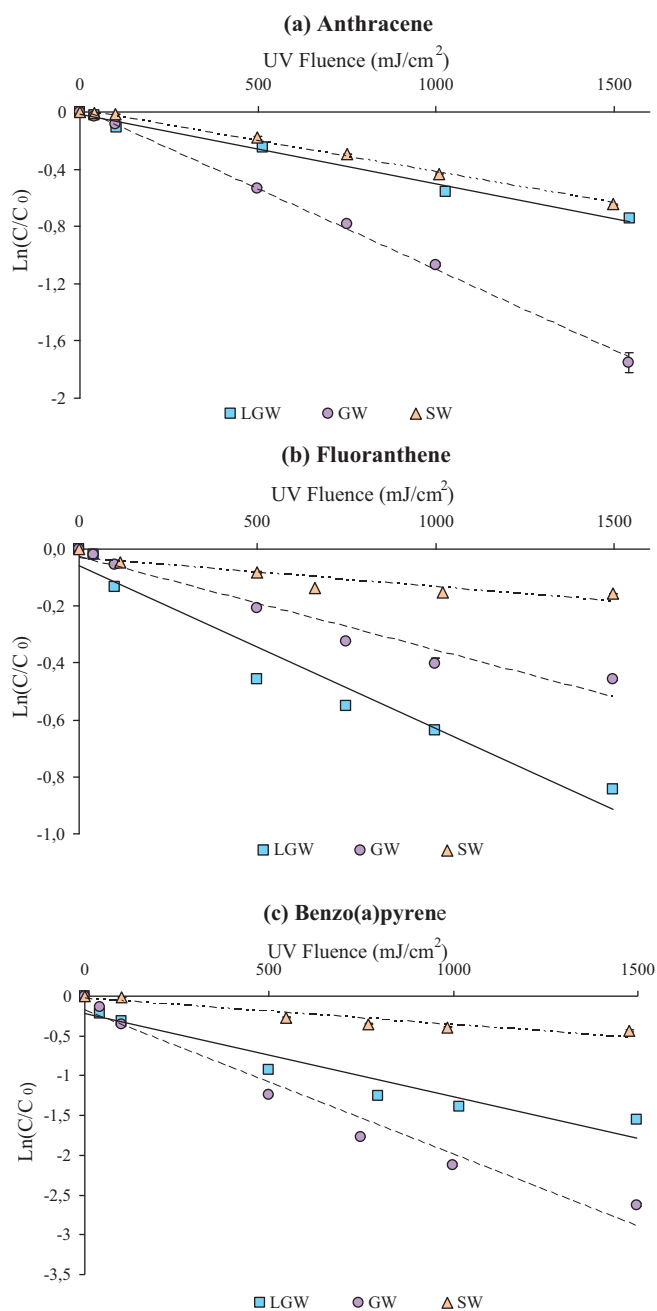

(c) Benzo(a)pyrene

Fig. 1. Ln(C/C_0) as a function of the UV fluence obtained for the LP/UV photolysis of the selected PAHs in laboratory grade water (LGW), groundwater (GW), and surface water (SW): (a) anthracene, (b) fluoranthene, and (c) benzo(a)pyrene; experimental values are given with error bars.

as the ratio between the total number of molecules of compound degraded and the total number of photons absorbed by the solution due to the compound's presence [11,41] and was determined according to Eqs. (3) and (4).

$$-\frac{d[PAH]}{dt} = k_t[PAH] = \left(\sum_\lambda K_s(254\ \mathrm{nm})\right)\phi[PAH] \quad (3)$$

$$K_s(254\ \mathrm{nm}) = \frac{E_p^o(254\ \mathrm{nm})\varepsilon(254\ \mathrm{nm})[1 - 10^{-a(254\ \mathrm{nm})z}]}{a(254\ \mathrm{nm})z} \quad (4)$$

where $K_s(254\ \mathrm{nm})$ is the specific rate of light absorption by the compound, $E_p^o(254\ \mathrm{nm})$ is the incident photon irradiance determined taking into account the radiometer meter reading as well as Petri,

Table 2
Decadic molar absorption coefficient (ε) at 254 nm and quantum yield (ϕ) obtained for the PAHs anthracene, fluoranthene, and benzo(a)pyrene; literature values are given in parenthesis.

Compound	$\varepsilon_{254\,\mathrm{nm}}$ (M^{-1} cm^{-1})	ϕ (mol einstein^{-1})
Anthracene	1094 (1042) [16]	0.096 (0.182–0.241) [16]
Fluoranthene	311	0.447
Benzo(a)pyrene	1084	0.314 (0.043) [15]

reflection, water, and divergence factors, and z is the solution depth in the Petri dish (2.1 cm).

The molar absorption coefficient and quantum yield obtained at 254 nm for the selected PAHs are shown in Table 2, while the decadic molar absorption coefficients obtained at different wavelengths are shown in Fig. 2.

The overlap between the absorption spectra of the PAHs and the emission of the LP lamps (monochromatic light at approximately 254 nm), show that anthracene and benzo(a)pyrene are good candidates for LP/UV degradation. Fluoranthene showed the lowest molar absorption coefficient while the lowest quantum yield was determined for anthracene. Therefore, the higher fluence-based rate constants in laboratory grade water could be expected for benzo(a)pyrene, which presents high absorption coefficient and quantum yield values. The values obtained for anthracene are in good agreement with a previous study that reports a decadic molar absorption coefficient of 1042 M^{-1} cm^{-1} and quantum yield values that range from 0.182 to 0.241 mol einstein^{-1} under different experimental conditions at 254 nm [16].

The UV fluence and time-based pseudo-first order rate constants determined (k_f and k_t, respectively) are shown in Table 3.

In laboratory grade water, the time and fluence rate constants obtained presented the following order: $k_{\mathrm{anthracene}} < k_{\mathrm{fluoranthene}} < k_{\mathrm{benzo(a)pyrene}}$. Lower degradation rate constants were obtained in the direct photolysis experiments conducted in surface water for all the selected PAHs compared to the laboratory grade results. The surface water matrix effect on the photolysis of the PAHs was particularly observed for fluoranthene and benzo(a)pyrene, which are the compounds that present higher hydrophobicity and soil adsorption coefficient and are therefore, expected to adsorb more on the organic matter and suspended solids that may protect the compounds from UV photolysis.

Although the structure of the selected compounds is expected to influence their degradation behavior, the water matrix composition was also found to be extremely important in the photolysis results obtained. Fig. 3 presents the degradation percent of the selected PAHs obtained in the different water matrices tested using a UV fluence of 1500 mJ/cm^2.
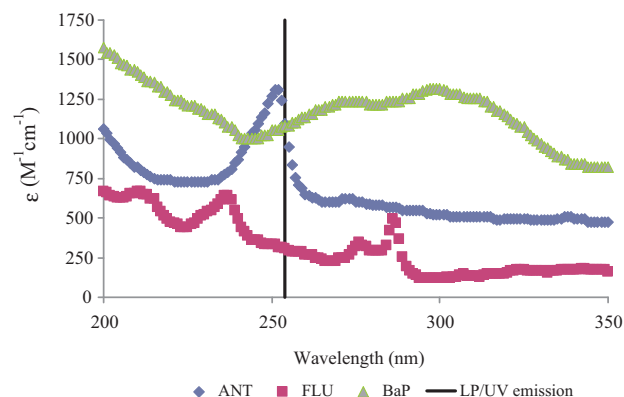

Fig. 2. Decadic molar absorption coefficient (ε) of anthracene (ANT), fluoranthene (FL), and benzo(a)pyrene (BaP) at a wavelength range of 200–350 nm.

Table 3
UV fluence-based LP/UV photolysis rate constants obtained for the selected PAHs in laboratory grade water (LGW), groundwater (GW), and surface water (SW); correlation coefficients are given in parenthesis.

Compound	k_f ($\times 10^{-4}$ cm²/mJ)			k_t ($\times 10^{-4}$ s⁻¹)		
	LGW	GW	SW	LGW	GW	SW
Anthracene	4.84 ± 0.25 (0.989)	11.28 ± 0.21 (0.996)	4.37 ± 0.08 (0.996)	0.85 ± 0.04 (0.989)	1.60 ± 0.03 (0.996)	0.57 ± 0.01 (0.996)
Fluoranthene	5.95 ± 0.41 (0.964)	3.23 ± 0.24 (0.951)	1.12 ± 0.18 (0.859)	0.93 ± 0.06 (0.964)	0.55 ± 0.04 (0.951)	0.16 ± 0.03 (0.859)
Benzo(a)pyrene	10.50 ± 0.91 (0.917)	18.15 ± 0.97 (0.967)	3.28 ± 0.35 (0.899)	1.13 ± 0.10 (0.917)	2.11 ± 0.11 (0.967)	0.30 ± 0.03 (0.899)

Even though higher percent degradations of anthracene and benzo(a)pyrene were obtained in groundwater rather than LGW, extremely high and similar removals were obtained in these matrices compared with the removals obtained in the surface water matrix. The rate constants trend obtained for fluoranthene in the different water matrices is in accordance with the composition of the water matrices in terms of organic matter and solids concentration. These results concur with a previous study conducted by Xia et al. [23], that reported that the fluoranthene photodegradation was accelerated with the decrease of the matrix fulvic acids concentration.

The degradation behavior of benzo(a)pyrene in laboratory grade water and surface water concur with a previous study in which a decrease was observed in the photolysis of benzo(a)pyrene in surface water when compared to laboratory grade water using a different UV lamp ($\lambda > 290$ nm) [22]. Fasnacht and Blough [22] compared the ratios between the photodegradation rate constants obtained in synthetic or real water matrices and the rate constants obtained in laboratory grade water for several PAHs. In that study [22], the matrix composition was found to affect the efficiency of anthracene degradation since the ratios of the rate constants obtained in synthetic and natural waters compared to laboratory grade water varied, from almost no effect reported in the Choptank River and Chesapeak Bay (ratios of 1.2 and 1.3, respectively) to a sensitized effect observed in the Atlantic Ocean (ratio obtained: 2.3). A sensitized effect was also observed for fluoranthene in a single surface water source tested (Choptank River).

The different light sources and compositions of the surface water matrices used in this study and in the study conducted by Fasnacht and Blough [22], may explain the differences observed in the degradation of the tested PAHs. However, both studies support the conclusions that differences in the composition of the different water matrices impact the degradation behavior of the selected PAHs and that within the same water matrix, different effects (inhibition and sensitization) may be observed for different PAHs. In our tested surface water matrix, inhibitory effects were observed compared to the spiked laboratory grade water that varied from a very slight to a very strong inhibitory effects observed for anthracene and flouranthene, respectively, whereas in groundwater, inhibitory effects were observed for flouranthene while sensitized effects were observed for benzo(a)pyrene and anthracene.

The effect of the water matrices composition on the photodegradation of the PAHs is very complex. Previous studies showed that the competitive photoabsorption of natural organic matter and dissolved organic carbon played an important role in the photodegradation of organic pollutants [27,28]. In addition, the electron-accepting (donating) potential of the water constituents may also influence the photodegradation of the PAH in the surface water matrix [42]. In this study, the ionic composition of groundwater is likely to be influencing the increase in the rate constants obtained for anthracene and benzo(a)pyrene. The groundwater matrix used showed a higher concentration of nitrates and a lower concentration of chloride than the surface water (Table 1). The effect of specific ionic water components on the degradation efficiency cannot be identified in this study because real water matrices were used. To further understand the influence of specific matrix components in the photolysis efficiency, future studies can be conducted using synthetic matrices spiked with different levels of ionic components as well as fulvic and humic acids. These studies are relevant and important but studies conducted in real water matrices provide better insight on what really happens in reality.

On the other hand, the higher natural organic matter content and dissolved organic material present in the surface water matrix are likely to be contributing to the decrease in the rate constants obtained for all the compounds due to the scavenging of the monochromatic UV light used. In a previous study conducted to address the photodegradation of pesticides using the same UV source this scavenging effect was not notorious [13]. This effect is probably more pronounced for the photolysis of PAHs due to their hydrophobic properties discussed above.

As shown in Fig. 3, low pressure UV photolysis was not very efficient for the removal of fluoranthene from groundwater and surface water (37% and 13%, respectively) while it proved to be efficient in the removal of anthracene and benzo(a)pyrene, specially in the groundwater matrix. The lower photolysis efficiency observed for fluoranthene is likely to be related to the fact that this compound does not strongly absorb radiation at 254 nm (Fig. 2). Therefore, although LP/UV lamps may prove to be efficient for drinking water treatment of the selected micropollutants, the results should be compared with the degradation efficiency obtained using other types of UV lamps that may enhance photolysis. In the present study, the percent degradations shown in Fig. 3 for anthracene, fluoranthene, and benzo(a)pyrene were obtained after approximately 2.5–3.2 h, 2.5–2.9 h, and 3.6–4.5 h of irradiation, respectively. These times varied with the composition of the water matrix and correspond to a UV fluence of 1500 mJ/cm². Woo et al. [20] reported a complete degradation of anthracene in laboratory grade water in less than 25 min using a lamp emitting radiation at 365 nm. A negligible degradation was obtained for fluoranthene in laboratory
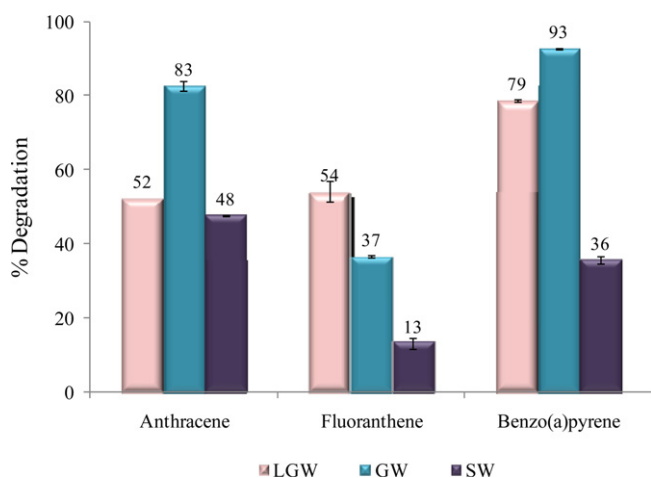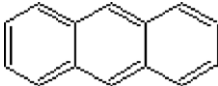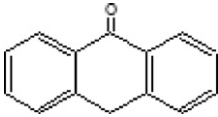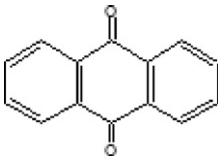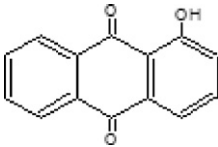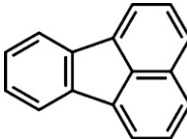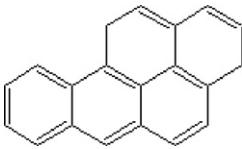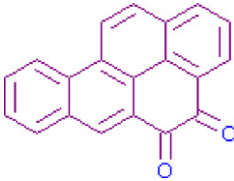

Fig. 3. % degradation of the selected PAHs at a UV fluence of 1500 mJ/cm² in laboratory grade water (LGW), groundwater (GW), and surface water (SW); experimental values are given with error bars.

Table 4
Studied compounds and by-products identified after photolysis.

Compound	Structure	Formula and MW	Retention time (min)	m/z (relative abundance)
Anthracene (parent compound)		$C_{14}H_{10}$ 178	20.1	178(100), 176(39), 89(21)
Anthrone		$C_{14}H_{10}O$ 194	27.9	194(89), 165(100), 163(20)
Anthraquinone		$C_{14}H_8O_2$ 208	28.6	208(100), 180(99), 152(86), 76(47)
1-Hydroxy-anthraquinone		$C_{14}H_8O_3$ 224	30.9	224(100), 168(58), 139(77)
Fluoranthene (parent compound)		$C_{16}H_{10}$ 202.3	30.5	202 (100) 200 (76) 203 (69)
Benzo(a)pyrene (parent compound)		$C_{20}H_{12}$ 252	39.4	252(100), 250(75), 126(57)
4,5-Benzo(a)pyrenedione		$C_{20}H_{10}O_2$ 282	38.8	282(0.2), 255(100), 226(23)

grade water after 3.3 h of irradiation with a lamp emitting radiation higher than 290 nm [22]. For benzo(a)pyrene, a degradation of 60% was obtained in laboratory grade water after approximately 4 min using radiation higher than 290 nm [22] while almost complete degradation was observed after 90–150 s using a low pressure lamp [15]. The efficiency to degrade the selected PAHs obtained in this study and in the other studies mentioned above suggests that LP/UV lamps may be better to degrade anthracene and benzo(a)pyrene than the other lamps that have already been tested while other lamps may be more suitable for the degradation of fluoranthene. However, even though some of these studies addressed the degradation efficiency of PAHs using other light sources, the photolysis results were always described as a function of time, which provides insight on the efficiency of different systems to degrade the compounds but cannot be compared directly with published results obtained under different experimental setups [33]. Furthermore, the photolysis efficiency to degrade anthracene, fluoranthene, and benzo(a)pyrene might be improved by advanced oxidation processes, which have, in some cases, proven to be more efficient than the direct photolysis [43].

Table 4 shows a summary of the photolysis by-products identified by mass spectrometry in the different water matrices after LP/UV exposure using a UV fluence of 1500 mJ/cm^2.

Even though photolysis by-products were not detected for fluoranthene, three products (anthrone, anthraquinone, and 1-hydroxy-anthraquinone) are produced by photolysis of anthracene, and one (4,5-benzo(a)pyrenedione) is produced by photodegradation of benzo(a)pyrene. Anthrone and anthraquinone have been previously reported to form as a consequence of anthracene degradation using lamps with an emission peak of 365 nm in the presence of titanium dioxide [20]. Although no chemical oxidant or catalyst was used in this study to induce advanced oxidation processes, oxygenated products were produced. This observation was previously reported by other authors. Haag and Hoigné [44] stated that the electronically excited singlet molecular oxygen may be formed as a consequence of light absorption of dissolved organic materials that may transfer energy to dissolved oxygen. Miller and Olejnik [15] proposed possible photolysis reactions of the PAH molecules surrounded by water with dissolved oxygen. The three main initial pathways reported for the degradation of PAHs were through

Table 5

Percent area of identified by-products formed relative to the area of the parent compounds in surface and groundwater matrices after photolysis of anthracene and benzo(a)pyrene using a UV fluence of 1500 mJ/cm^2.

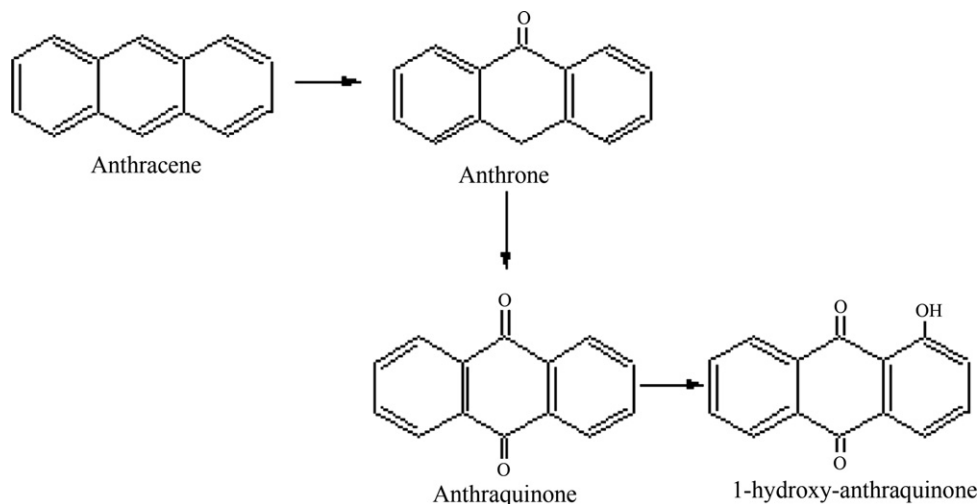|	% relative to parent compounds			
	Compound	Surface water prior to UV	Surface water after UV	Groundwater prior to UV	Groundwater after UV
Photolysis	Anthracene	100	100	100	100
	Anthraquinone	0.4	52	1.4	284
	Anthrone		0.4		2.6
	1-hydroxy anthraquinone		2.1		27.9
B(a)P photolysis	Benzo(a)pyrene	100	100	100	100
	4,5-Benzo(a)pyrenedione		20.1		245

Fig. 4. Anthracene photolysis by-products formation.

radical cation and due to the presence of oxygen, via singlet oxygen formation and via hydroxyl radical formed in reactions from a superoxide anion.

Table 5 shows a comparison between the detection of the identified compounds in the groundwater and surface water matrices prior to and following LP/UV exposure (using a UV fluence of 1500 mJ/cm^2). The detected by-products are reported in terms of the percentage change of their area relative to the area of the parent compound photodegraded.

The presence of 4,5-benzo(a)pyrenedione was detected after LP/UV photodegradation of the surface and groundwater samples spiked with benzo(a)pyrene (Table 5). This by-product is formed at a much higher proportion relative to the parent compound in the groundwater samples compared to the surface water samples, showing that the matrix composition may considerably affect the production of photolysis by-products. The same trend was observed for the production of all by-products produced in the photodegraded samples initially spiked with anthracene (Table 5). Prior to UV exposure of the anthracene samples, anthraquinone was found to be present in the surface and groundwater matrices. However, the area percentage of this compound and of other compounds undetected in the untreated samples (anthrone and 1-hydroxy anthraquinone) increased considerably after photolysis showing that these compounds are formed due to the photodegradation of anthracene. A possible pathway that results from the photodegradation of anthracene is shown in Fig. 4.

Photolysis by-products of anthracene and benzo(a)pyrene are expected to form using the tested UV fluences. The products formed were all oxygenated compounds that could be even more toxic than the parent compounds [17,18,45–47]. Since mineralization of the target compounds was not attained, future studies should therefore focus on an evaluation of the combined toxicity effects considering the parent compounds decrease and the photolysis by-products formation, to support the feasibility of the treatment. In addition, other UV sources such as medium pressure lamps and higher UV fluences should also be tested to evaluate whether mineralization of the parent compounds and photolysis by-products formed can be achieved.

Direct photolysis using low pressure lamps can be expected to decrease the levels of PAHs in different water matrices, especially in groundwater. However, by-product production was found to be matrix related and by-products of anthracene and benzo(a)pyrene were found to be formed at a higher proportion relative to the parent compounds in the groundwater matrix.

Acknowledgments

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