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Incubation of solid state C₆₀ fullerene under UV irradiation mimicking environmentally relevant conditions



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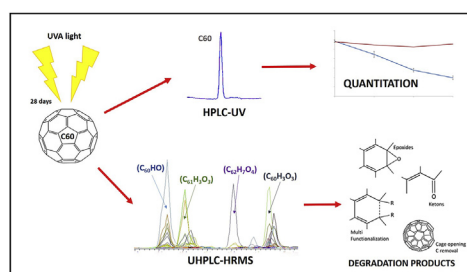
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HIGHLIGHTS

- C₆₀ fullerene at the solid state was irradiated with UVA light for a period of 28 days.
- A C₆₀ solution was either dried onto a glass surface or spiked into quartz sand or sandy soil samples.
- C₆₀ losses followed a pseudo-first order reaction rate, with half-lives ranging from 0.8 d to 13.1 d.
- C₆₀-like products consisting of functionalized fullerenes structures were detected.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon-based nanomaterials, such as C₆₀ fullerenes, are expected to accumulate in soil due to direct release and deposition from the atmosphere. However, little is known about the environmental fate of these nanoparticles which may be susceptible to photochemical and microbial degradation. In the present work, C₆₀ was incubated for a period of 28 days and irradiated with UVA light. Three experiments were carried out where the fullerenes were either spiked onto a glass surface or added to quartz sand or sandy soil samples. At specific time intervals the samples were extracted and analysed by liquid chromatography coupled to UV or high resolution mass spectrometric (HRMS) detection. The fullerenes were degraded in all the treatments and the decay followed a pseudo-first-order rate law. In absence of a solid matrix, the half-life ($t_{1/2}$) of the C₆₀ was 13.1 days, with an overall degradation of 45.1% that was accompanied by the formation of functionalized C₆₀-like structures. Furthermore, mass spectrometric analysis highlighted the presence of a large number of transformation products that were not directly related to the irradiation and presented opened cage and oxidized structures. When C₆₀ was spiked into solid matrices the degradation occurred at a faster rate ($t_{1/2}$ of 4.5 and 0.8 days for quartz sand and sandy soil, respectively). Minor but consistent losses were found in the non-irradiated samples, presumably due to biotic or chemical processes occurring in these samples. The results of this study suggest that light-mediated transformation of the fullerenes will occur in the environment.

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1. Introduction

Fullerenes, including C₆₀, are a class of carbonaceous nanomaterials displaying a closed-cage structure composed of five- and

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six-membered rings of carbon (Kroto et al., 1985). Due to their innovative properties, the production and application of these compounds is developing rapidly and fullerene-based consumer products are already commercially available (Hendren et al., 2011; Maynard and Michelson, 2012). Increased production and use will inevitably lead to an increased release into the environment and there is concern for the possible negative effects on humans and the ecosystem. Although fullerenes can occur naturally (e.g. lightning strikes, wildfires, e.g. Howard et al., 1991) or be unintentionally produced, (e.g. as by-products of combustion or during oil refinery, e.g. Utsunomiya et al., 2002; Tiwari et al., 2016), as a result of their large scale production, the potential release of purposefully manufactured nanomaterials is expected to play a major role in determining the occurrence of these novel contaminants in the environment. In this context, C₆₀ released in the environment is expected to accumulate in soil more than in water and the atmosphere (Gottschalk et al., 2009). In particular, fullerenes may enter the terrestrial environment directly as a consequence of their use and disposal as well as due to amendment of soil with bio-solids (Navarro et al., 2013) and indirectly by deposition from the atmosphere (Laitinen et al., 2014; Tiwari et al., 2016).

Although little is known about their environmental fate, fullerenes may undergo functionalization, polymerization, degradation and mineralization reactions due to the interaction with ozone, biota and solar radiation (Panina et al., 1997; Lee et al., 2009; Avanası et al., 2014; Tiwari et al., 2014). With regard to their photochemistry, fullerenes are well known to be photosensitive and to absorb light in the UV range (Carboni et al., 2013). In particular, interaction of the fullerenes with UV-A light, which represent the main UV irradiation reaching the Earth surface, will likely play a major role in determining their environmental fate (Hwang and Li, 2010). Previous studies have shown that C₆₀ dissolved in organic solvent (e.g. benzene) undergo photo-oxidation with consequent formation of epoxides, oxides and more polar unidentified products (Taylor et al., 1991; Wood et al., 1991; Creegan et al., 1992), whereas photo-polymerization was observed under oxygen-limiting conditions (Sun et al., 1995). Oxidative pathways were also observed in water when C₆₀ was in the form of suspended nano-aggregates, nC₆₀, and irradiated by UV-A (Hwang and Li, 2010), UV-C (Lee et al., 2009) or sunlight (Hou and Jafvert, 2009). In particular, studies carried out at environmentally relevant conditions reported half-lives from 19 to 41 h and surface functionalization of C₆₀ (oxygenation and hydroxylation) as well as the formation of unidentified water soluble intermediates. However, most of the research was focused on fullerenes dissolved in solvents. To the best of our knowledge, no research was conducted yet that irradiates C₆₀ nanoparticles dispersed onto a surface or into a solid matrix (e.g. soil), which may represent the main form in which these nanoparticles are present in the environment.

The characterization of transformation pathways for fullerenes is challenging because of the large number of possible products that they may create (e.g. polymerization, functionalization and cage break-down) (Taylor et al., 1991; Hwang and Li, 2010) and possible strategies have been recently reviewed by Pycke et al. (2012). In particular, spectroscopic detection is an effective tool for the analysis of fullerenes, due to the strong absorptivity of these chemicals in the UV range. Furthermore, since both the fullerenes and the functionalized structures display absorption in the same range (i.e. circa 330 nm) spectroscopic detection may help in the identification of the total levels of the species in a sample (Carboni et al., 2013). Mass spectrometric analysis can instead provide structural information needed for the identification of transformation products resulting from fragmentation (Lee et al., 2009) and oxidation (Tiwari et al., 2014). In this context, high resolution mass spectrometry (HRMS) was successfully employed for the

detection of fullerenes and functionalized fullerenes, also in environmental matrices (Astefanei et al., 2014). In the present work, the fate of fullerenes at environmentally relevant conditions was studied by incubating C₆₀ for a period of 28 days. The fullerenes were spiked in solid matrices and the effect of UVA light irradiation was investigated.

2. Materials and methods

2.1. Reagents and chemicals

Toluene (analytical grade), methanol (ULC/MS grade) and acetonitrile (LC-MS grade) were obtained from Biosolve B.V. (Valkeniswaard, The Netherlands). Fullerenes C₆₀ (purity >99.9%, CAS: 99685-96-8) and C₇₀ (purity >99%, CAS: 115383-22-7) were purchased from Sigma-Aldrich (Steinheim, Germany). Stock solutions of the individual fullerenes were prepared in toluene at a concentration of 500 mg/L and placed on an orbital shaker (Laboshake orbital shaker, Gerhardt, Königswinter, Germany) in the dark overnight. Further solutions needed for the experiments were obtained by dilution of the stock solutions and stored at 4 °C in the dark and sonicated for 2 min before use (Bransonic 12, Branson, Danbury CT, United States). Quartz sand (silicon dioxide, SiO₂) was purchased from Sigma-Aldrich (Zwijndrecht, the Netherlands). The sandy soil consisted of a fullerenes free top-soil (top 10 cm) collected in a natural park in Oude Schulpweg, Castricum, the Netherlands (52° 32' 39.689"N, 4° 39' 5.623"E). This soil had previously been characterized by our group and had no detectable fullerenes (Carboni et al., 2016b) and 0.2% organic carbon (Carboni et al., 2016a). The soil was placed in an oven at 65 °C for one week in order to remove traces of water and then sieved with a 1.68 mm mesh.

2.2. Sample preparation and incubation

The sample preparation took place into a fume hood, and the laboratory windows were equipped with UV-filters. For the preparation of the samples, 100 µl of a C₆₀ solution in toluene (10 mg/L) was spiked at the centre of the glass Petri dishes. The spiking of toluene solutions was preferred over the spiking of aqueous fullerene suspensions since the latter necessarily contain functionalized fullerene structures (i.e. oxides; Murdianti et al., 2012) that may hamper the characterization of transformation products resulting from the irradiation. Then the dishes were covered with the quartz domes (custom made) and the solvent allowed to evaporate for 30 min. Quartz sand and sandy soil samples were prepared as following: 2 ml of a C₆₀ solution in toluene (20 mg/L) were spiked into 100 g of sample that was then homogenized by stirring and allowed to dry. Then 300 g of sample were added while stirring in order to obtain a final mass of 400 g of sample at the concentration of 100 µg/kg of C₆₀. Subsequently, 10 g were placed in the glass dishes, resulting in a sample thickness of circa 1.5 mm. The incubation took place in a 1 m² area provided with three UV lamps (UVP, Keswick, Australia) set at 365 nm and placed at a height of 80 cm. This resulted in a uniform irradiation of UVA light (350–390 nm range) whose maximum intensity was 9 µW/cm²/nm at circa 360 nm (Fig. S1 in Supplementary info). The light measurements in the incubator were achieved with the aid of a USB2000+ spectrometer and the Spectrasuite software (both Ocean Optics, Duiven, The Netherlands). Non-irradiated samples were placed into the incubator and covered with aluminium foil in order to prevent exposure to light. The incubator was covered with a 100% obscurant curtain and the temperature was held constant at 25 ± 0.5 °C.

2.3. Extraction and analysis

The samples ($n = 3$) from each treatment were extracted at the beginning of the experiment and at specific time intervals of 1, 3, 7, 14 and 28 d. These time intervals were chosen according with the results of a preliminary experiment in which C_{60} , spiked into sandy soil and irradiated with UV-A light, showed concentrations below the limit of quantification after 28 d of incubation (data not shown). The extraction proceeded as following: the samples were taken out of the incubator and 50 μ l of a C_{70} solution in toluene (internal standard, 10 mg/L) were added. After equilibration time of 30 min, 5 ml of toluene was used for the rinsing of the petri dishes and then transferred into a 10 ml vial. The procedure was repeated twice. In the case of quartz sand and sandy soil, the samples were homogenized by stirring after spiking of the internal standard and underwent extraction with the protocol previously described by our group (Carboni et al., 2013). The extracts were analysed with the HPLC-UV method described in Carboni et al. (2013) with minor modifications. Briefly, the method employed a pyrenylpropyl silica stationary phase (Buckyprep), whereas the mobile phase consisted of toluene and acetonitrile. Elution was achieved with an isocratic method employing a 80:20 toluene:acetonitrile mixture. Quantification was based on the chromatographic peak areas as described in the supplementary info. The UHPLC-HRMS analyses were performed using an UHPLC system (Nexera, Shimadzu, Den Bosch, The Netherlands) equipped with a binary pump, autosampler and column oven. Briefly, the retention of the chemicals was achieved with a core-shell Kinetex 2.6 μ m biphenyl 100 Å chromatographic column (Phenomenex, Utrecht, the Netherlands) consisting of a biphenyl stationary phase whereas methanol (A) and toluene (B) were used as mobile phase (Carboni et al., 2016a). A gentle elution program was used to enhance separation of compounds with varying polarity range: from 0 to 5 min B was kept at 0%, following a linear increase to 75% at 21 min and a final holding step until 25 min. The flow rate was set to 0.4 ml/min, whereas the column temperature was kept at 30 °C. The MS methodology was adopted from Carboni et al. (2016a). Mass detection was carried out with a high resolution Quadrupole-Time of Flight mass spectrometer (Q-TOF; maXis 4G equipped with HD collision cell, Bruker Daltonics, Wormer, The Netherlands) coupled to the UHPLC system described earlier. Compounds were ionized using an Ion Booster electrospray ionization source (IB-ESI) operating in negative mode using the following settings: capillary voltage 1000 V, end plate offset -400 V, charging voltage 300 V, dry heater 200 °C, nebulizer gas 4.1 bar and dry gas 3 l/min. Nitrogen was used for ionization and as collision gas, and obtained from a N_2 generator (Avilo, Dirksland, The Netherlands). Ion transfer settings were as follows: funnel radio frequency (RF) 325 Vpp (voltage point to point) and multipole RF 300 Vpp. Mass calibration was achieved as reported by Carboni et al. (2016a) with minor modifications as described in the supplementary info. The collision cell RF, transfer time and prepulse storage time were varied within four time segments throughout the analysis. Mass spectra were recorded at 2 Hz with a range of 50–2000 m/z . The first two segments (segments 1 and 2) were dedicated to low and high masses calibration, respectively. Consequently, compounds eluting within the first ten minutes (segment 3), i.e. displaying relatively higher polarity, were measured with settings optimized for low masses whereas non-polar compounds eluting after ten minutes (segment 4) were analysed with settings optimized for high masses. Fragmentation data of the most intense peaks were automatically acquired with Auto MS/MS mode using a maximum cycle time of 3 s. Smart exclusion and active exclusion were enabled to limit acquisition of continuous background and increase uniqueness of precursor selection, respectively. More information regarding the MS settings for the segments and Auto MS/

MS are reported in the supplementary info. An extensive list of masses was compiled from background compounds found in solvent and sample blanks, and set as exclusion masses (± 0.05 Da window) to improve the quality of mass spectra. Unknown transformation products (TPs) in a sample were screened and identified according with a five step procedure. First, a list of chromatographic peaks of interest was compiled from manual inspection of base peak chromatograms and by use of the software based Auto MS/MS peak finder. Secondly, for each peak of interest, a list of masses of interest was manually generated from averaged mass spectra. For these masses, an extracted ion chromatogram (EIC) was generated to verify its origin from the chromatographic peak. Thirdly, a candidate list of chemical formulas was created based on accurate mass (≤ 5 ppm deviation) and isotopic fit (≤ 50 mSigma) with SmartFormula. Fourthly, candidates were removed if present in solvent or sample blanks. Finally, tentative identification of candidates was performed from MS/MS fragmentation data, if present. Mass spectral data were processed with DataAnalysis 4.3 (Bruker Daltonic, Wormerveer, The Netherlands).

3. Results and discussion

3.1. Incubation

Losses of C_{60} fullerenes occurred during irradiation with UV-A light in all the experiments performed, as shown in Fig. 1. Furthermore, similar to what was observed by Hwang and Li (2010) when irradiating aqueous C_{60} with UV-A light, the decay of the

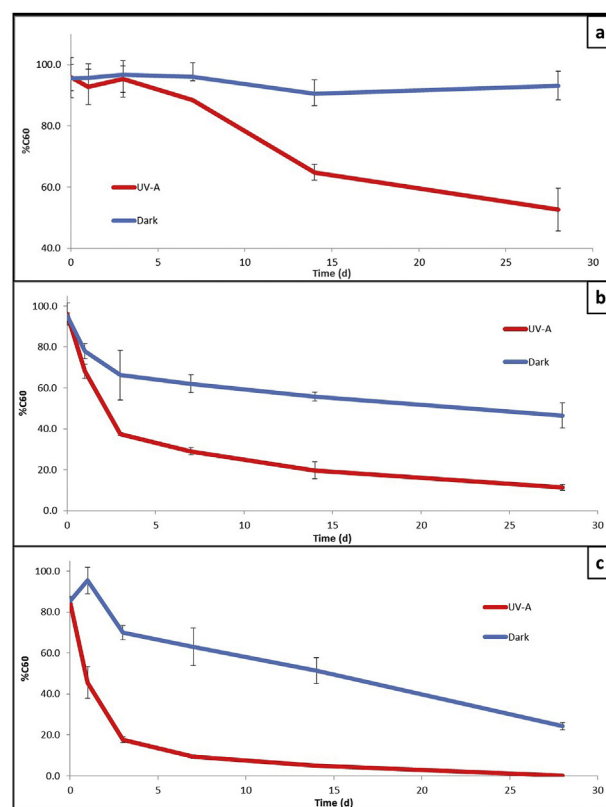


Fig. 1. Concentration of C_{60} fullerenes over time in (a) fullerenes dried on top of a glass surface ("glass"), (b) spiked into quartz sand and (c) spiked into sandy soil at the concentration of 100 μ g/kg. The red line represents the sample irradiated with UV-A light whereas the blue line represents the samples incubated in the dark. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fullerenes followed a pseudo first order reaction rate in all the irradiated treatments ($r^2 \geq 0.85$, Table 1).

When the C_{60} was added onto glass dishes (“glass” in the further manuscript), degradation of the fullerenes started after 3 d and a total loss of 45.1% was observed after 28 d of incubation (Fig. 1a). The negligible losses in the non-irradiated glass samples indicate that, similar to what was previously reported in water (Hwang and Li, 2010; Hou and Jafvert, 2009) and organic solvents (Taylor et al., 1991), the degradation of the C_{60} was due to a photochemical process. These results suggest that fullerenes released in the environment might be degraded by the ultraviolet portion of the solar radiation. However, it must be noted that the half-life of 13.1 d in the glass incubation was much longer than those previously reported for the dissolved C_{60} , estimated in the range of 10–40 h (Hou and Jafvert, 2009; Taylor et al., 1991), and could be explained by the lower reactivity of the fullerenes in the solid state in comparison with the dissolved structures or a role of the solvent in the process.

When C_{60} was spiked into solid matrices, the observed losses in the irradiated samples were higher and reached 88.1% and 100% for quartz sand and sandy soil, respectively (Fig. 1b and c), at the end of the incubation. These correspond to half-lives of 4.5 and 0.8 days, respectively (Table 1), and suggest that other processes took place, in addition to the irradiation, that enhanced the degradation in these samples. Especially in the sandy soil samples, the matrix-enhanced loss may be explained with a biotic degradation due to microorganisms present in the soil or by other processes such as a matrix-related photosensitisation (e.g. due to organic matter, Nkhilia et al., 2014). Thus, these results indicate that once deposited onto soil, the fate of fullerenes will be mostly determined by other factors than the irradiation. This is supported by the fact that, in contrast to the glass incubation, the degradation of the fullerenes started at the beginning of the incubation and that consistent losses over time were found also in absence of light (Table 1). In particular, also the decay of C_{60} in the non-irradiated samples followed a pseudo first order reaction rate ($r^2 \geq 0.80$) with half-lives of 14.3 and 6.7 days for quartz sand and sandy soil, respectively.

3.2. Transformation products

3.2.1. C_{60} -like products

In contrast to the HPLC-UV chromatograms, which were dominated by the C_{60} and C_{70} peaks (Fig. S7 in Supplementary info), UHPLC-HRMS chromatograms revealed the presence of additional peaks (Fig. 2a). In particular, three structures, namely “C60-I”, “C60-II” and “C60-III”, showed accurate masses and isotopic cluster distributions equal to that of C_{60} , but eluted later at retention times 19.2, 20.0 and 22.5 min, respectively (Fig. 2a and c).

These products could not be characterized in the present work and their composition has not been elucidated yet. However, the detection of a C_{60} cage structure might suggest the presence of surface functionalized fullerenes undergoing in-source fragmentation during the ionization process. Modification of the ionization

method with regard to the source temperature and capillary voltage (i.e. to promote a ‘softer ionization’) did not lead to the identification of the precursor masses and resulted in a near or complete loss of the signal. The detection of $C_{60}O_n$ traces together with the C_{60} -like peaks (Fig. S8 in Supplementary info), suggests that these products may consist of oxidized products similar to those observed by Tiwari et al. (2014) who recently reported the elution of C_{60} oxides ($C_{60}O$, $C_{60}O_2$ and $C_{60}O_3$) to occur after that of C_{60} with a methodology similar to that of the present work (i.e. reverse phase chromatography with functionalized silica stationary phase). Quantitation of these structures was hindered by the lack of analytical standards. However, the analysis of the peak areas showed that, in the glass incubation samples, the decrease in concentration of C_{60} corresponded to the increase of the C_{60} -like transformation products over time (Fig. 3). In particular, the abundance of all the structures increased from the baseline signal after 3 d of incubation, in correspondence with the decrease of C_{60} , and reached a maximum after 14 d. The decrease to lower levels at the end of the incubation suggests the formation of intermediates in the transformation of fullerenes irradiated with UV-A light. It must be noted that, in quartz sand and sandy soil extracts, these products were either not detected or did not show a different trend between irradiated and non-irradiated treatments. This could be due to several reasons, including 1) different processes (e.g. biotic transformation) that took place in the solid matrices, 2) the extraction of these chemicals was hindered by the sample matrix and/or 3) the products were degraded at a faster rate and were already removed at the first sampling step.

3.2.2. Unknown products

Auto MS/MS analysis (see Section 2.3) highlighted the presence of several structures that eluted immediately before C_{60} , between 12.2 and 14.4 min (Fig. 2b), and will be referred as “unknowns” in the further manuscript. An example of the Auto MS/MS analysis is provided in the supplementary info (Fig. S9). In general, base peaks were identified as the most abundant traces at a certain retention time and, within each base peak, several m/z traces were automatically selected for MS/MS. A tentative identification of the unknowns was based on the MS1 and MS2 accurate masses and isotopic cluster distribution, but complicated by the low signals intensity and the co-elution of more structures. Furthermore, in-source fragmentations may have occurred similar to what was reported above (Section 3.2.1). A summary of the m/z values relative to the unknowns found in the glass incubation is reported in Table 2 with a tentative identification of their chemical formula.

Analysis of the mass spectra highlighted an ionization mechanism (i.e. the formation of a radical molecular ion $[M]^{\bullet+}$) and isotopic cluster distribution similar to that of the fullerenes. Furthermore, the mass-to-charge ratio (m/z) was always larger than that of the C_{60} , suggesting functionalization of the carbon cage. The addition of carbon was always in the form of $(CH_3O)_n$ groups and has already been reported to occur as a consequence of the formation of adducts with methanol (Kolkman et al., 2013). However,

Table 1
Degradation characteristics derived from photolysis experiments with C_{60} fullerene. The results of the UVA irradiated and non-irradiated (dark) incubations are reported on the left and right side of the table, respectively.

	UV-A				Dark			
	$t_{1/2}$ (d)	k (d^{-1})	r^2	% Loss (28 d)	$t_{1/2}$ (d)	k (d^{-1})	r^2	% Loss (28 d)
Sandy soil	0.80	0.375	0.921	100	6.69	0.045	0.971	71.8
Quartz sand	4.49	0.067	0.846	88	14.33	0.021	0.800	51.3
Glass	13.09	0.023	0.951	45.1	301.03	0.001	0.405	2.4

$t_{1/2}$: half-lives, k : pseudo-first-order reaction constant, r^2 : regression coefficient.

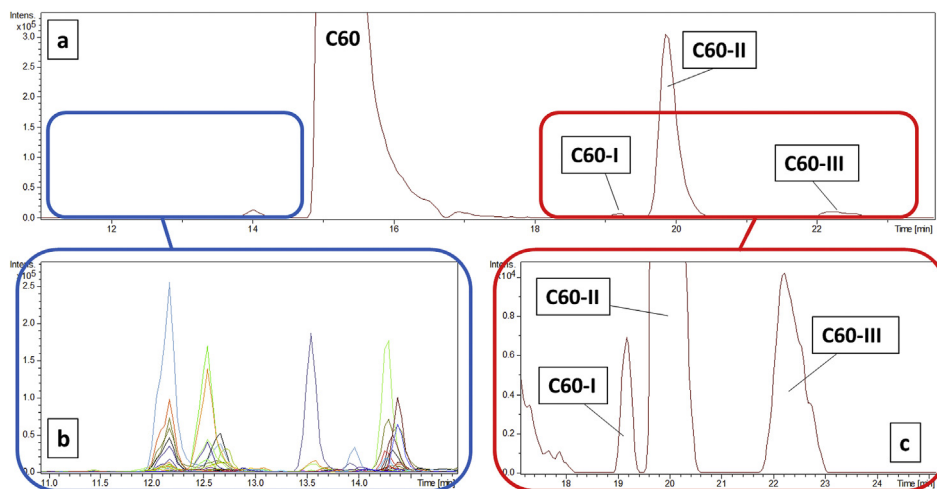


Fig. 2. UHPLC-HRMS analysis of glass incubation samples irradiated with UV-A light. (a) Chromatogram presenting the C_{60} peak at retention time 15 min and smaller C_{60} -containing peaks (C60-I, C60-II and C60-III) eluting later. (b) Several unknown peaks eluting before C_{60} (blue frame). (c) A zoom of the 18–24 min range (red frame), highlighting the presence of the C_{60} -containing (C_{60} -like) structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

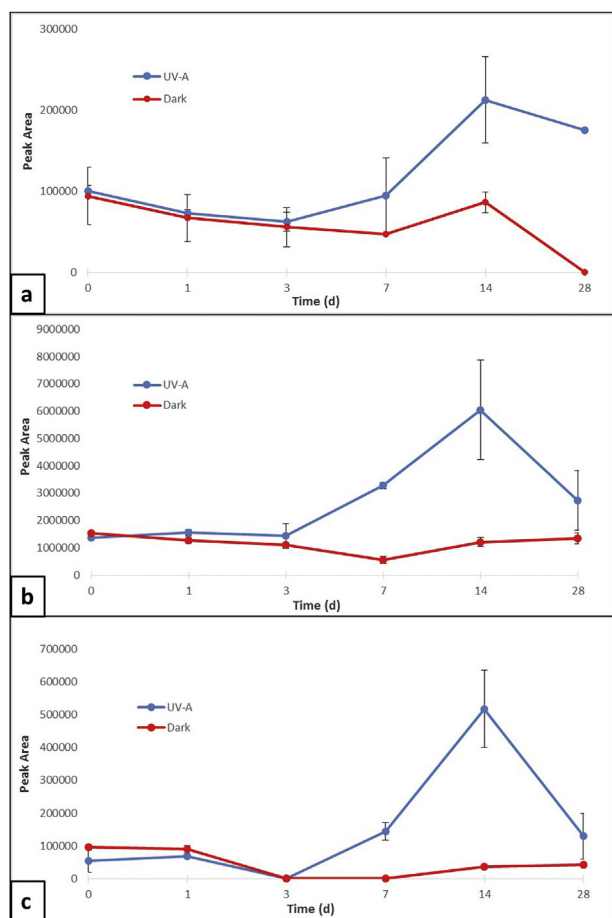


Fig. 3. Abundance (peak area) over time of (a) C60-I, (b) C60-II and (c) C60-III products in the glass incubation. The blue and red lines represent the irradiated (UV-A) and non-irradiated (Dark) samples, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

since the methodology applied in the present work is less prone to the formation of adducts in comparison with other ESI-MS techniques (Carboni et al., 2016a), the (CH_3O) clusters may suggest a

methoxylation of the fullerenes. This hypothesis is supported by the fact that the number of (CH_3O) additions were not associated with all the transformation products detected. On the other hand, carbon loss occurred with the formation of both C_{59} and C_{58} species. The loss of carbon, and specifically C_2 units, has already been observed in the mass spectrometric analysis of functionalized C_{60} (e.g. fullerols; Chao et al., 2011) and indicates the opening of the cage.

Additional functionalization mostly consisted of hydrogen and oxygen that could be located in hydroxylic, ketone and epoxide groups. We found no evidence of clusterization of the fullerenes, such as the formation of $C_{120}O$ observed by Taylor et al. (1998). These results indicate that the unknowns found in the present work could be similar to those observed during UV and sunlight irradiation of C_{60} dissolved in water and organic solvents (Taylor et al., 1991; Hou and Jafvert, 2009; Lee et al., 2009). Similar to the C_{60} -like structures (see Section 3.2.1), the unknowns were more abundant in absence of a matrix. However, the analysis of the peak areas did not show a direct correlation between irradiation of the samples and their concentrations. Although not present in the spiking solutions and non-spiked samples (Fig. S10 in Supplementary info), some of the products were found to be already present at the beginning of the incubation and may have been formed during the sample preparation. Furthermore, some unknowns increased in abundance in the non-irradiated treatment only (Fig. S11 in Supplementary info) indicating that some processes either did not occur in presence of light or that the products were too short-lived to be detected at the time intervals in the present study. Finally, it must be noted that no evidence of transformation products was found at the beginning of the chromatograms (between 0 and 12 min) where the more polar species are expected to elute. This could be due to a limitation of the present method that did not allow their detection or, similar to what reported by Taylor et al. (1991), that too polar products may not have been extracted with toluene. In general, alternative methodologies should be tested that may overcome the limitations of this work. In particular, we recommend 1) the use of higher concentrations that, although not mimicking environmental conditions, would simplify the determination of the fulleroid species in the samples, 2) a first step of extraction with a more polar solvent in order to recover polar products that were likely excluded in this work and 3) improve identification by the use of alternative MS ionization

Table 2
Summary of the unknown products found in the glass incubation. The base peak indicates the most abundant structure detected in MS1 at a certain retention time (Rt). Within each base peak, some *m/z* traces were automatically selected (Auto MS/MS) in MS1 and sent to the MS2. The collision energy was set at 100 eV.

Rt (min)	Base peak (<i>m/z</i>)	MS1 Precursor ion (<i>m/z</i>)	MS2 Product ions (relative abundance (%)) (<i>m/z</i>)
12.18	737.0033 (C ₆₀ HO)	720.0003 (C ₆₀)	→ 719.9980(C ₆₀ , 100%)
		737.0030 (C ₆₀ HO)	→ 719.9976(C ₆₀ , 35%); 735.9923(C ₆₀ O, 60%); 737.0002(C ₆₀ HO, 5%)
		767.0128 (C ₆₁ H ₃ O ₂)	→ 719.9983(C ₆₀ , 11%); 735.9923(C ₆₀ O, 80%); 767.0104(C ₆₁ H ₃ O ₂ , 4%); 768.9854(C ₆₀ HO ₃ , 5%)
12.55	783.0085 (C ₆₁ H ₃ O ₃)	783.0085 (C ₆₁ H ₃ O ₃)	→ 695.9979(C ₅₈ , 2%); 723.9934(C ₅₉ O, 23%); 735.9900(C ₆₀ O, 27%); 739.0160(C ₆₀ H ₃ O, 13%); 751.9875(C ₆₀ O ₂ , 20%); 752.9923(C ₆₀ HO ₂ , 22%); 767.9814(C ₆₀ O ₃ , 3%)
		735.9949 (C ₆₀ O)	→ 720.0004(C ₆₀ , 5%); 723.9930(C ₅₉ O, 81%); 735.9940(C ₆₀ O, 14%)
12.68	735.9949 (C ₆₀ O)	735.9949 (C ₆₀ O)	→ 719.9993(C ₆₀ , 3%); 723.9910(C ₅₉ O, 50%); 735.9900(C ₆₀ O, 7%); 739.9880(C ₅₉ O ₂ , 30%); 751.9882(C ₆₀ O ₂ , 16%)
		751.9882 (C ₆₀ O ₂)	→ 695.995(C ₅₈ , 2%); 719.9984(C ₆₀ , 21%); 723.9926(C ₅₉ O, 21%); 735.9917(C ₆₀ O, 25%); 751.9879(C ₆₀ O ₂ , 31%)
12.75	875.0913 (C ₆₅ H ₁₆ O ₅)	751.9879 (C ₆₀ O ₂)	→ 719.9972(C ₆₀ , 24%); 740.9945(C ₅₉ HO ₂ , 12%); 751.0158(C ₆₁ H ₃ O, 35%); 782.0329(C ₆₂ H ₆ O ₂ , 6%); 783.0391(C ₆₂ H ₇ O ₂ , 11%); 813.0529(C ₆₃ H ₉ O ₃ , 9%); 845.0791(C ₆₄ H ₁₃ O ₄ , 1%); 875.0937(C ₆₅ H ₁₆ O ₅ , 2%)
		875.0158 (C ₆₅ H ₁₆ O ₅)	→ 723.9917(C ₅₉ O, 9%); 727.9836(C ₅₈ O ₂ , 4%); 739.0131(C ₆₀ H ₃ O, 8%); 752.9979(C ₆₀ HO ₂ , 56%); 783.9747(C ₆₀ O ₄ , 4%); 784.0139(C ₆₁ H ₄ O ₃ , 19%)
		831.0287 (C ₆₂ H ₇ O ₄)	→ 726.0046(C ₅₉ H ₂ O, 1%); 728.9965(C ₅₈ HO ₂ , 2%); 740.995(C ₅₉ HO ₂ , 13%); 756.9901(C ₅₉ HO ₃ , 26%); 767.9822(C ₆₀ O ₃ , 10%); 784.0139 (C ₆₂ H ₇ O ₄)
14.05	799.0019 (C ₆₁ H ₃ O ₄)	799.0012 (C ₆₁ H ₃ O ₄)	→ 739.9881(C ₅₉ O ₂ , 73%); 767.9818(C ₆₀ O ₃ , 3%); 768.0181(C ₆₁ H ₄ O ₃ , 13%); 799.0012(C ₆₁ H ₃ O ₄ , 11%)
		719.9984 (C ₆₀)	→ 719.9984(C ₆₀ , 100%)
14.3	751.0203 (C ₆₁ H ₃ O)	751.0203 (C ₆₁ H ₃ O)	→ 719.9986(C ₆₀ , 35%); 751.0141(C ₆₁ H ₃ O, 28%); 752.9955(C ₆₀ HO ₂ , 37%)
		771.0065 (C ₆₀ H ₃ O ₃)	→ 727.9895(C ₅₈ O ₂ , 4%); 739.9883(C ₅₉ O ₂ , 42%); 755.9837(C ₅₉ O ₃ , 6%); 767.0100(C ₆₁ H ₃ O ₂ , 3%); 771.0065(C ₆₀ H ₃ O ₃ , 45%)
14.4	802.0266 (C ₆₁ H ₆ O ₄)	802.0266 (C ₆₁ H ₆ O ₄)	→ 735.9925(C ₆₀ O, 7%); 739.9873(C ₅₉ O ₂ , 27%); 755.9801(C ₅₉ O ₃ , 5%); 767.0106(C ₆₁ H ₃ O ₂ , 9%); 771.006(C ₆₀ H ₃ O ₃ , 49%); 802.0222(C ₆₁ H ₆ O ₄ , 3%)

Rt: retention time.

conditions and/or interfaces to avoid in-source fragmentation of precursor ions.

In general, the results of the present work show that fullerenes will be degraded in the environment and that the removal from the soil compartment could be relatively fast. In this context, the data hereby presented will be helpful for modelling and environmental studies. In particular, we have shown that the assessment of fullerenes fate and occurrence is complicated by the formation of a large number of transformation products that will likely display different properties in comparison with the original structures (e.g. enhanced mobility). Thus, future research addressing these topics will need screening analysis such as those hereby presented in order to identify the totality of the species present in environmental samples as well as to further elucidate the pathways of degradation in the environment.

4. Conclusions

The effect of UV-A light irradiation on fullerenes incubated at the solid state was investigated. When C₆₀ was directly irradiated, i.e. in absence of a matrix, the irradiation had a clear effect on the degradation. However, when the C₆₀ was spiked into a quartz sand or sandy soil samples, much faster degradation occurred suggesting that, once deposited onto the soil, their fate will more likely be determined by other factors such as the interactions with soil materials and microbiota, including bioturbation and biotransformation. The results indicate that fullerenes could undergo an oxidative pathway similar to that observed for C₆₀ dissolved in water, and can result in the break-down of the carbon cage. The present study highlighted the complexity of these processes and the need for analytical strategies for their understanding. For instance, less selective methodology, such as UV detection, can be suitable for the quantitation of the total concentrations of fullerenes in the samples, whereas HRMS-based techniques are required for the characterization of the many species that likely result from their transformation. Nevertheless, the results hereby presented

will be helpful in the assessment of the environmental fate of fullerenes and in defining future strategies for their study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.01.149>.

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