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Incubation of solid state C_{60} fullerene under UV irradiation mimicking environmentally relevant conditions

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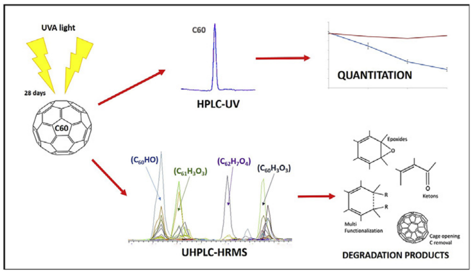
HIGHLIGHTS

- C_{60} fullerene at the solid state was irradiated with UVA light for a period of 28 days.
- A C_{60} solution was either dried onto a glass surface or spiked into quartz sand or sandy soil samples.
- C_{60} losses followed a pseudo-first order reaction rate, with half-lives ranging from 0.8 d to 13.1 d.
- C_{60}-like products consisting of functionalized fullerenes structures were detected.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon-based nanomaterials, such as C_{60} 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, C_{60} 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 C_{60} was 13.1 days, with an overall degradation of 45.1% that was accompanied by the formation of functionalized C_{60}-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 C_{60} 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.

1. Introduction

Fullerenes, including C_{60}, 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, C_{60} 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; Avanasi 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 C_{60} 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 C_{60} was in the form of suspended nano-aggregates, nC_{60}, 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 C_{60} (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 C_{60} 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 C_{60} 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. (Valkenswaard, The Netherlands). Fullerenes C_{60} (purity >99.9%, CAS: 99685-96-8) and C_{70} (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, SiO_2) 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 C_{60} 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 fullerenes suspensions since the latter necessarily contain functionalized fullerenes 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 C_{60} 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 C_{60}. 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 m^2 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 $\mu W/cm^2/nm$ 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.