



Analysis of fullerenes in soils samples collected in The Netherlands[☆]



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ABSTRACT

Fullerenes are carbon based nanoparticles that may enter the environment as a consequence of both natural processes and human activities. Although little is known about the presence of these chemicals in the environment, recent studies suggested that soil may act as a sink. The aim of the present work was to investigate the presence of fullerenes in soils collected in The Netherlands. Samples ($n = 91$) were taken from 6 locations and analyzed using a new developed LC-QTOF-MS method. The locations included highly trafficked and industrialized as well as urban and natural areas. In general, C₆₀ was the most abundant fullerene found in the environment, detected in almost a half of the samples and at concentrations in the range of ng/kg. Other fullerenes such as C₇₀ and an unknown structure containing a C₆₀ cage were detected to a lower extent. The highest concentrations were found in the proximity of combustion sites such as a coal power plant and an incinerator, suggesting that the nanoparticles were unintentionally produced during combustions processes and reached the soil through atmospheric deposition. Consistent with other recent studies, these results show that fullerenes are widely present in the environment and that the main route for their entrance may be due to human activities. These data will be helpful in the understanding of the distribution of fullerenes in the environment and for the study of their behavior and fate in soil.

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1. Introduction

Fullerenes are carbon based nanomaterials widely researched due to their unique properties that make them useful for a large number of applications, including electronics and optics as well as medicine and personal care products (Murayama et al., 2004; Mauter and Elimelech, 2008; Osawa, 2002). Moreover, the possibility to derivatize the closed cage carbon structure, with consequent production of novel nanomaterials, widens the range of uses of these chemicals (Hummelen et al., 1995). Although the annual production is estimated to be tens of tons per year, a large increase is expected in the near future (Piccinno et al., 2012; Hendren et al., 2011), which is likely to imply higher emissions into the

environment. Thus, fullerenes are nowadays referred to as emerging contaminants and there is concern about the environmental and health implications that may arise. In particular, fullerenes may be released directly during production or they may leach from materials as a consequence of their use and disposal. Furthermore, they may be produced in combustion processes and therefore associated with both natural phenomena (e.g. forest fires, volcanic eruptions; Heymann et al., 1994; Howard et al., 1991) and human activities such as industrial processes (e.g. as a byproduct during combustion of carbonaceous materials) and transport (e.g. fuel combustion; Murr et al., 2004).

Little is known about the fate of these chemicals once they end up in the environment. Although some studies suggested that fullerenes may be degraded due to both biotic and abiotic processes (e.g. Tiwari et al., 2014), others highlighted the stability of C₆₀ that may result in their accumulation in the environment (Jehlicka et al., 2005; Parthasarathy et al., 2008; Avanasri et al., 2014; Navarro et al., 2016). However, fullerenes have been shown to affect soil organisms (e.g. earthworms, Van der Ploeg et al., 2011), hence,

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monitoring studies are crucial in order to provide valuable information about the occurrence of these chemicals and to determine the potential environmental risk associated with them.

In general, pristine structures such as C₆₀ and C₇₀ are expected to be more abundant in the environment because of the higher production volumes and their higher natural occurrence. Furthermore, they could result from the degradation of functionalized structures such as methanofullerenes and fullerol (e.g. due to fullerol mineralization, Navarro et al., 2016). Indeed, several studies reported the presence of C₆₀ and C₇₀ fullerenes in environmental matrices (Sanchis et al., 2012, 2013; 2015; Núñez et al., 2012; Astefanei et al., 2014), whereas functionalized structures (i.e. engineered nanomaterials) were seldom detected (Astefanei et al., 2014).

Soil has been predicted to be a sink for fullerenes (Gottschalk et al., 2009) that may enter the terrestrial environment via atmospheric deposition, direct release, water transport and amendment of soils (Sanchis et al., 2012; Navarro et al., 2013). However, most of the research so far has been focused on water and wastewater samples (Farré et al., 2010; Astefanei et al., 2014; Emke et al., 2015; Núñez et al., 2012; Van Wezel et al., 2011; Kolkman et al., 2013) and data regarding the occurrence of fullerenes in soil are limited to a few studies. In particular, Sanchis et al. (2013) reported the presence of fullerenes in soils from Saudi Arabia associated with the petroleum refinery activities in the area. In their study, C₆₀ was the only compound detected, and was found in 19% of the samples at concentrations in the low µg/kg range. Fullerenes were detected to a larger extent (67.6% of the agricultural soils and 91% of the urban soils) during a monitoring study in Brazil where both C₆₀ and C₇₀ were found at concentrations up to 154 ng/kg (Sanchis et al., 2015). In this case, their presence was also correlated to combustion activities, particularly the deposition of atmospheric particulate resulting from combustion processes. Fullerenes were also found in aerosol particulates (Sanchis et al., 2012) and urban atmosphere (Laitinen et al., 2014) as well as resulting from coal combustion (Utsunomiya et al., 2002), suggesting that atmospheric deposition could represent a main route for their entrance in the terrestrial environment.

In the present work, an environmental survey was carried out with the aim of investigating the presence of fullerenes in soil samples collected in The Netherlands. For this purpose, a method employing Ultra High Performance Liquid Chromatography (UHPLC) coupled with High Resolution Mass Spectrometric (HRMS) detection was used (Carboni et al., 2016). The main goal was to investigate the presence of C₆₀ and C₇₀ in highly trafficked and industrialized areas, i.e. those areas where the generation of fullerenes may be related to human activities, in order to assess the influence that these possible sources may have in the occurrence of these chemicals in the environment. The selection of the samples was done in order to represent diverse situations. Thus, soil samples were collected in proximity of expected sources such as a coal power plant (Utsunomiya et al., 2002) as well as in potentially uncontaminated areas (i.e. natural park).

2. Materials and methods

2.1. Reagents and chemicals

Toluene, methanol, isopropanol and acetonitrile (Biosolve, Valkenswaard, The Netherlands) were all analytical grade (LC-MS). Fullerenes C₆₀ (CAS: 99685-96-8) and C₇₀ (CAS: 115383-22-7) standards were purchased by Sigma-Aldrich (Steinheim, Germany). Stock solutions of the individual fullerenes, at the concentration of 5 mg/L, were prepared in toluene 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).

2.2. Sample collection and treatment

The surface soil samples (top 5 cm, at least 125 g each) were collected in 250 ml amber glass bottles. Each sample consisted of the composite of five sub-samples (25–30 g each) collected at the corners and centre of a 1 m² squared area. A total of 91 surface soils were sampled in 6 locations in The Netherlands:

Location A was an urban area in proximity of a coal power plant in Amsterdam (15 samples, labelled A_01 - A_15); Location B was a rural and urban area nearby the AVR incinerator in Duiven (16 samples, labelled B_01 - B_16); Location C was an area surrounding the Amsterdam's "Ring" highway (26 samples, labelled C_01 - C_25); Location D was in green areas (e.g. parks, flower beds) in the city of Amsterdam (16 samples, labelled D_01 - D_16); Location E was a natural park situated near Castricum (6 samples, labelled E_01 - E_06) whereas Location F samples were collected in proximity of a runway at the Eindhoven airport (12 samples, labelled F_01 - F_12). Additional information regarding the distance of the sampling locations from the expected sources and their coordinates are reported in the [Supplementary information](#). The wind direction was assumed as the main wind direction recorded during the three days before the sampling was performed. The samples were placed in a freezer at -20 °C overnight and lyophilized with a Scanvac Coolsafe freeze-dryer (Labogene, Lyngø, Denmark) in order to remove traces of water. The dried samples were ground and homogenized with an agate mortar and sieved before undergoing extraction with the protocol already reported by our group (Carboni et al., 2013) with minor modifications, i.e. the temperature was set at 20 ± 2 °C as recommended by Perez et al. (2013) and the extraction was performed in 40 ml custom made glass vial in order to allow the extraction of larger volumes. Briefly, circa 25 g of each sample underwent two cycles of extraction with toluene with each cycle consisting of a combination of sonication for 20 min with a Bransonic 12 ultrasonic bath (Branson, Danbury CT, United States) and shaking for 2 h (Laboshake orbital shaker, Gerhardt, Königswinter, Germany). Negative controls consisted of silicon dioxide samples (25 g each) extracted and analyzed with the same procedure. The extracts were stored in a refrigerator at 4 °C in the dark and sonicated for 30 s before to be analyzed.

2.3. Sample analysis

The analyses were performed with the method recently developed in our research group for the identification of fullerenes in soil and sediment samples as described previously (Carboni et al., 2016), using an UHPLC system (Nexera, Shimadzu, Den Bosch, The Netherlands) equipped with a binary pump, autosampler and column oven. Retention of the chemicals was achieved with a core-shell Kinetex 2.6 µm biphenyl 100 Å chromatographic column (Phenomenex, Utrecht, the Netherlands) consisting of a biphenyl stationary phase. The UHPLC system was coupled to a high resolution Quadrupole-Time of Flight mass spectrometer (Q-TOF; maXis 4G, Bruker Daltonics, Wormer, The Netherlands) equipped with an Ion Booster electro spray (IB-ESI) ionization source (Bruker Daltonics, Wormer, The Netherlands) as described elsewhere (Carboni et al., 2016). High purity nitrogen was used as collision gas (Avilo, Dirsland, The Netherlands). Automatic mass calibration was performed for each sample by injecting a 2 mM sodium acetate solution at the beginning of the chromatographic run. Additional information regarding the analytical set up and

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