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Distribution of fullerenes (nC_{60}) between sediment and water in freshwaters

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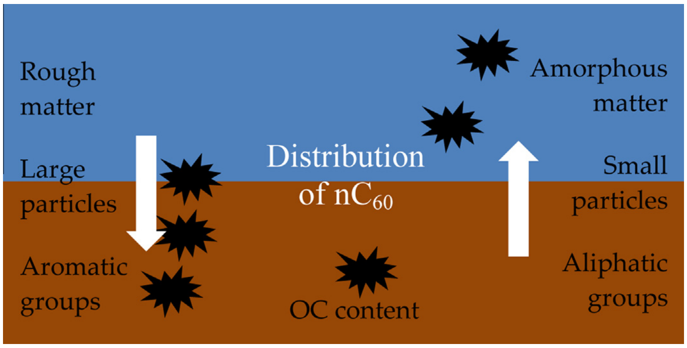
HIGHLIGHTS

- Distribution of nC_{60} in the sediment surface layer was determined.
- The fate of nC_{60} depends on chemical character and fine structure of sediment.
- Bottom sediments retain fullerenes but a portion may remain mobile.

GRAPHICAL ABSTRACT



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ABSTRACT

Depending on environmental conditions, fullerenes (nC_{60}) have the potential to settle to the bottom sediments. In this study the distribution of nC_{60} was investigated in the labile zone between sediment and water. Three freshwater–sediment systems representing oligohumic, mesohumic, and polyhumic lakes with varying sediment composition and structure were used to investigate the target of fullerenes. The largest portion of water suspended fullerenes was found in the sediment, but a part re-suspended relatively quickly to water-stabile particles associated with natural particles. Rapid initial re-suspending was followed by a slower one offering a continuous pathway to the water phase. Re-suspending was highest from the sediment with a high amount of amorphous matter, small particles and a highly aliphatic character, amounting to 9 ± 1% of the initial amount of fullerenes, whereas it was 4 ± 1% in aromatic sediments with larger particles and less amorphous matter. These results indicate that bottom sediments can retain fullerenes but a portion may remain mobile depending on sediment character. Re-suspended fullerenes may again be available to aquatic species—this knowledge should thus be taken into account in the environmental risk assessment of fullerenes.

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1. Introduction

The carbon nanoparticle fullerene-C_{60} is widely researched for various applications from electronics to medicine and cosmetics due to its unique properties. There is no reason to assume that the manufacturing and use of fullerenes is achieved without any discharges, while increasing production raises the risk of C_{60} reaching the environment. Additionally, fullerene molecules seem to be relatively protected from environmental and biological degradation (Kümmerer et al., 2011), indicating that they can be expected to remain in the environment for a long time and may accumulate.

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Therefore, their potential environmental risks need to be understood.

Some applications offer fullerenes a straight way to the aquatic environment via waste waters (Benn et al., 2011). Fullerenes have also been found in waste water effluents (Farré et al., 2010; Benn et al., 2011). Depending on environmental conditions, fullerenes have the potential to target different entities in aquatic environments (e.g. Pakarinen et al., 2013). Although fullerenes are insoluble in water (less than 10^{-9} mg L^{-1}, Ruoff et al., 1993) they can form water-soluble colloidal agglomerates (nC_{60}) created in water flow and mixing (Brant et al., 2005). These agglomerates are typically 25–500 nm in size and may remain in the water phase for several months or even years (Chen et al., 2004). Water-stability facilitates fullerene mobility and makes them more available for aquatic organisms. Remaining in the water phase also enhances the possibility of nC_{60} being degraded by sunlight into smaller agglomerates (Hou and Jafvert, 2009). There is also the potential of photochemical transformations on surfaces of agglomerates (Qu et al., 2010) or their conversion into vinyl ether, products containing carboxyl and carbonyl, and fulleroles (Hou et al., 2010). All these changes can alter the toxic potential of nC_{60}—a reason to investigate the fate of fullerenes in aquatic environments.

In natural conditions nC_{60} likely interacts with other abundant particles and colloids, such as dissolved natural organic matter (DNOM) (Gao et al., 2009), which complicates assessing their environmental fate. Interactions with natural particles may enhance water stability of fullerenes (e.g. Chen and Elimelech, 2008; Xie et al., 2008; Pakarinen et al., 2013) by, e.g., forming a steric barrier due to binding them by π–π interactions to DNOM, and preventing agglomeration in this manner (Casadei et al., 2007). In addition, changes in polarity on particle surfaces caused by DNOM may enhance water stability. Nevertheless, steric stability caused by DNOM has been suggested to be more significant than changes in surface polarity (Mashayekhi et al., 2012).

In addition to water stability, some water characters, such as small DNOM molecular size, high amount of carboxylic groups in DNOM (Pakarinen et al., 2013), and high ionic strength, especially Ca^{2+} concentration, allow fullerenes to settle to the bottom sediments (Chen and Elimelech, 2008). Thus, ecological risks of fullerenes also reach benthic species along with aquatic ones. Association with natural particles can also alter toxicity and the intake of fullerenes on organisms, which increases the importance of investigating interactions between nC_{60} and natural matrices.

Most investigations concerning fullerenes' fate in aquatic environments have focused on the water phase. Although sediment has been modelled to be a sink of fullerenes (Gottschalk et al., 2009) only a limited number of publications explore the interactions between fullerenes and sediment or soil. Nevertheless, those interactions are critical in their environmental fate (Zhang et al., 2012a,b). Sediment is not a final sink for many traditional chemicals (Baker, 1991), and it cannot be assumed that it is for fullerenes either. "Storage" potential of traditional chemicals in the sediment depends on the characters of sediment, water, and the chemical itself. These characteristics may also affect the behaviour of fullerenes. Sediment surface is especially susceptible to mixing by water flows and bioturbation caused by benthic species. Thus, fullerenes in the sediment may become re-suspended to water, remaining mobile and available for aquatic species (Pakarinen et al., 2011).

The current study mimicked a situation where fullerenes have been released to water and modified agglomerates. The subject of investigation was fullerenes' targeting the labile zone between sediment and water. The study covers fullerenes' behaviour in three freshwater–sediment systems representing oligohumic, mesohumic, and polyhumic lakes with a varying composition and sediment structure. Firstly, the potential of water-suspended fullerenes to adhere to sediment was studied. Secondly, the potential of fullerenes to become re-suspended by the water flows was determined. Thirdly, characters of sediments affecting adhering and re-suspending processes were mapped.

2. Materials and methods

2.1. Chemicals and experimental waters

Crystalline C_{60}-fullerene (purity at least 98%) was obtained from Sigma–Aldrich, USA; an extensive characterization of C_{60}, including thermo gravimetric analysis and quantification of metal impurities was published recently (Waissi-Leinonen et al., 2012). Natural freshwater sediments were collected from Lake Höytiäinen (62°41′21″ N), Lake Kuorinka (62°37′48″ N, 29°23′49″ E), and Lake Mekrijärvi (62°45′ N, 30°57′ E) in eastern Finland. These sediments were chosen because they are nearly pristine with no industry in nearby areas (Sormunen et al., 2008, 2009). The sediments were sieved to a particle size of less than 1 mm to exclude large particles and debris, stored at 5 °C and protected from light prior to testing. Characteristics of the sediments are listed in Table 1 and particle size distributions in Fig. 1. Artificial freshwater (AFW) used for preparing the fullerene suspensions and overlying water phases of systems was synthesized by adding analytical grade salts (Baker, Netherlands): $CaCl_2 \times 2H_2O$ 58.8 mg L^{-1}, $MgSO_4 \times 2H_2O$ 24.7 mg L^{-1}, $NaHCO_3$ 13.0 mg L^{-1}, and KCl 1.2 mg L^{-1}; hardness $[Ca^{+2}] + [Mg^{+2}] = 0.5$ mM) to Millipore water (at least 18.2 mΩ) and adjusting the pH to 6.8. This artificial freshwater corresponds to Finnish lakes in terms of its pH and hardness. The toluene used in extractions was purchased from Baker (Netherlands), and NaCl from WVR International (France), both were analytical grade. Formvar polyvinyl resin for coating electron microscopy grids was obtained from SPI Supplies (USA).

2.2. Preparation and characterization of nC_{60}

Crystalline fullerenes were suspended to artificial freshwater (AFW) using a stirring method (Brant et al., 2005) to produce nC_{60} agglomerates. Stock suspensions of nC_{60} were made by adding 100 ± 0.1 mg of crystalline fullerenes into 500 mL of AFW and performing magnetic stirring at 1000 rpm for 4 weeks at 20 ± 2 °C. The suspension was protected from light with an aluminium foil. For concentration measurements, fullerenes were extracted to toluene and their absorbance was measured at 335 nm with a spectrophotometer (Cary 50 bio, Mulgrave, Australia) (Tervonen et al., 2010). Concentrations were calculated on a standard curve (fit for linearity $r^2 > 0.999$, six points). The efficiency of this extraction method was verified with a total organic carbon analyser (Shimadzu TOC-5000A with ASI-5000A auto sampler, Japan)—it was 98 ± 2% for nC_{60} in AFW. Recoveries for extractions of nC_{60} in sediment–water mixtures were calculated

Table 1
Characteristics of the test sediments. Uncertainties represent standard deviations.

	Lake Kuorinka	Lake Höytiäinen	Lake Mekrijärvi
Dry weight % $n = 4$	24.9 ± 0.5	12.2 ± 2.1	9.7 ± 0.7
Organic carbon % $n = 3$	1.64 ± 0.11	3.2 ± 0.02	24.28 ± 0.17
Nitrogen % $n = 3$	0.07 ± 0.01	0.23 ± 0.01	1.26 ± 0.02
C:N ratio	23.4	13.9	19.3
Particle size (nm) $n = 400$	2265 ± 1540	1712 ± 1113	1046 ± 1267
Characters of OC[a]	Aromatic	Aromatic	Aliphatic
Classification of lake[b]	Oligohumic	Mesohumic	Polyhumic

[a] Based on ^{13}C-CPMAS NMR studies. The characters are described relatively between used sediments because percentage portions of each functionality could be determined only from the Lake Mekrijärvi sediment.

[b] Classified on the basis of DOC concentration (Särkkä, 1996).

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