

How Redox Conditions and Irradiation Affect Sorption of PAHs by Dispersed Fullerenes (nC60)

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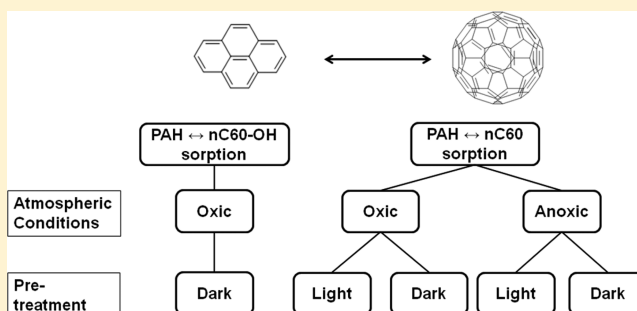
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S Supporting Information

ABSTRACT: Surface properties, dispersion state, and sorption behavior of carbon-based nanomaterials will change after being released into the environment. To study these processes, five different scenarios were considered to probe the impact of changes in surface properties of dispersed fullerenes (nC60) on their sorption potential due to irradiation and presence of oxygen. Sorption isotherms of pyrene by nC60 were determined at environmentally relevant concentrations applying a passive sampling method. Isotherms of all dispersion scenarios were best fit with the Dubinin–Ashthakov model. Sorption was strongest for nC60 kept under anoxic condition. Both the presence of oxygen and irradiation significantly decreased the sorption capacity of nC60, while commercially available polyhydroxy fullerenes had the smallest sorption. In addition, competition for sorption sites was never observed in multiple sorbate experiments with four polycyclic aromatic hydrocarbons at small concentration. A strong relationship between sorption coefficients and hydrophobic properties of sorbates suggests that hydrophobic interactions are of major importance. The results emphasize that aging of released fullerenes results in a reduced strength of interactions with nonpolar compounds and, thus, reduces the impact on the environmental transport of hydrophobic pollutants.



INTRODUCTION

Research on carbon-based nanomaterials (CNM) has been increasing over the past decade due to their unique physicochemical properties (e.g., large surface area to volume ratio). The question of their fate and impact on the environment has also become a major concern due to an expected rise in production of these materials in the future.¹ Even though there is consensus that CNM will eventually reach the environment, their environmental behavior and impact on the fate of other pollutants remains controversial. Predicted fullerene (C60) concentrations (e.g., 0.02 and 0.04 ng/L in surface waters in Europe and Switzerland, respectively²) are likely to increase in the future. This fact substantiates the need of further research on the environmental impact of CNM.

The hydrophobic property of fullerenes (C60) results in the formation of aggregates when C60 is aqueously dispersed. Numerous studies have shown that environmental factors may influence the dispersion of aqueous of fullerenes (nC60) due to changes in surface properties. These changes may result from oxidation (e.g., after exposure to sunlight) or other, non-covalent, surface modifications (e.g., due to the presence of natural organic matter (NOM)).^{3–6} These obvious effects of aging on dispersion properties will inevitably influence the environmental behavior of nC60. The consequences of these changes in surface chemistry on their sorption behavior are yet

poorly understood. Recently, Gai et al.⁷ showed that sorption of atrazine by nC60 was significantly affected by the dispersion method applied. However, there was no consistent correlation between sorption of atrazine and nC60 particle size. In another study, pH and ionic strength (i.e., NaCl) had no major influence on the sorption of polycyclic aromatic hydrocarbons (PAHs) by nC60, whereas the addition of NOM decreased freely dissolved PAHs concentration.⁸ These inconsistent trends between sorbent particle size and their sorption may be assigned to the difference in probe sorbates investigated. Furthermore, irradiation was shown to disaggregate nC60 clusters and form products of smaller hydrophobicity via an oxidative pathway without carbon mineralization.⁹ Possible impact(s) of oxidation of nC60 on their sorption potential have not yet been investigated. However, such information is essential as potential surface oxidation represents an important aging factor influencing the impact of fullerenes once they are released to natural systems. Very recently, possible solar

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transformation of nC60 was proposed to be a critical step for assessing the environmental impact after a potential release into surface waters.¹⁰

The very limited information on the sorption behavior of partially/fully dispersed nC60 systems might be explained by difficulties associated with the generally applied batch sorption test setups. In sorption batch experiments, solid and liquid phases are generally separated by centrifugation, sedimentation, or filtration. Most CNM suspended in aqueous solution may easily be separated from the aqueous phase as they tend to form aggregates due to their hydrophobicity. However, a fraction of dispersed CNM may remain in solution and cause an underestimation of determined distribution coefficients. We thus used a passive sampling technique to accurately measure sorption coefficients applying polyoxymethylene (POM-SPE), which has recently been used to investigate sorption of PAHs by multiwalled carbon nanotubes (MWCNTs).¹¹ A complete phase separation when working with (partially) dispersed systems is assured by inserting a third phase into the system that can easily be separated. In addition, the POM-SPE method permits determining freely dissolved aqueous concentration of PAHs down to 1 pg/L.¹² Studying sorption over a wide concentration range allows a detailed investigation of sorption mechanisms of CNM through robust isotherm analysis. Moreover, sorption can be investigated at sorbate concentrations likely to be found in the environment. The objective of the present study was to analyze the impact of environmental factors (i.e., irradiation and presence of oxygen) known to alter nC60 surface properties on their sorption behavior toward PAHs. Sorption isotherm analysis and extensive solid phase characterization data were combined in order to better understand the interactions likely to occur in natural environments.

■ EXPERIMENTAL SECTION

Materials. Fullerenes (C60, 99.5% purity, Sigma-Aldrich, Steinheim, Germany) and polyhydroxy fullerenes (C60-(OH)_{18–22}, BuckyUSA, Houston, TX, USA) were used as purchased. A polyoxymethylene sheet (POM; thickness 0.5 mm; density 1.41 g/cm³) was purchased from Vink Kunststoffen BV (Didam, The Netherlands). The POM sheet was cut into pieces that were cold-extracted in an ultrasonic unit SONOREX SUPER RK106 (Bandelin, Berlin, Germany) once in *n*-hexane and three times in methanol (each for 30 min), and subsequently air-dried.¹³

Pyrene (Pyr, 99.5%) and Pyr-d10 (99.5%, internal standard for quantification) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Other PAHs (phenanthrene, Phen; benz[a]pyrene, BaP; and benz[a]anthracene, BaA) were obtained from Sigma-Aldrich (Steinheim, Germany). For quantification of multiple solute experiments, a mixture of deuterated PAHs ("PAH mix 31") containing acenaphthene-*d*₁₀ (99.5%), chrysene-*d*₁₂ (98.5%), naphthalene-*d*₈ (99.5%), perylene-*d*₁₂ (99.5%), and phenanthrene-*d*₁₀ (99.5%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All stock solutions were prepared in methanol. Selected properties of the sorbates are listed in Table S1 of the Supporting Information (SI). Acetone (for analysis), *n*-hexane, and methanol (both residual analysis grade) were purchased from Acros Organics (Geel, Belgium).

Preparation of nC60 Aging Scenarios. Approximately 20 mg of C60 and 7 mg of C60-OH were weighed into 50-mL and 20-mL borosilicate glass vials, respectively. Vials were then filled

with background solution containing 0.1 mmol NaCl, leaving minimal headspace, and subsequently closed with PTFE-lined caps. Four aging scenarios of varying irradiation and atmospheric conditions were prepared with C60. Half of the samples were shaken in the dark (nC60-D) or exposed to lamp light irradiation (nC60-L, two 15 W fluorescent ultraviolet bulbs, Sylvania T8 F15W/BL350, bulbs emitted light at a spectrum of 315–400 nm with a peak at 368 nm¹⁴). Note that previous studies on irradiation of fullerenes were performed in similar glassware and at similar wavelength.^{15,16} Each half of samples was further subdivided into two batches, one under oxic and the other under anoxic conditions (denoted with subscripts O and A, respectively). Based on previous results of Lee et al.⁹ and Hou and Jafvert,¹⁵ an irradiation time for pretreatment of 28 d was chosen. Hence, all samples (i.e., oxic and anoxic) were shaken horizontally for 28 d at 150 rpm. Anoxic samples were pretreated, spiked, and equilibrated in a glovebox under a constant atmosphere of nitrogen. The glovebox was flushed daily with fresh nitrogen to ensure anoxic conditions throughout the experiment. Anoxic NaCl background solution was prepared by autoclaving for 25 min, followed by cooling under nitrogen atmosphere. The solution was transferred to glass bottles sealed with aluminum screw caps and immediately stored in the glovebox.

The fifth scenario consisted of nC60-OH under oxic conditions and without light pretreatment.

POM-SPE Batch Experiments. POM pieces were added to the nC60 dispersions and pyrene was subsequently spiked at initial concentrations ranging from 0.1 to 1000 µg/L. To ensure reproducibility, two data points of each isotherm were prepared in duplicates. The amount of methanol was 0.2% (v/v) in all samples to minimize the cosolvent effect. Samples were subsequently shaken at 150 rpm in the dark for 28 d to achieve equilibration of the sorbate between the aqueous phase, POM, and nC60 (for further details on the POM-SPE method refer to the SI). Temperature was kept constant at 25 ± 1 °C during all experiments.

After equilibration, the sorbate concentrations in POM were determined. For this purpose, the POM pieces were withdrawn from the vials and wiped with a wet paper tissue to remove sorbent from POM surface (SI Figure S1). After the addition of the internal standard, the POM pieces were extracted with methanol by accelerated solvent extraction (ASE 200, Dionex USA; 1500 psi, 100 °C). Methanol was exchanged to hexane under N₂, samples were concentrated, and analyzed by GC-MS (Agilent 7890A gas chromatograph coupled 5975C mass spectrometer; HP-5 ms column (30 m × 250 µm × 0.25 µm, J&W Scientific), pulsed splitless mode, and oven program 55 °C for 1 min, then 15 °C/min up to 300 °C). Analyte quantification was achieved by single ion monitoring (SIM) mode.

The POM-SPE method was also used to determine the sorption coefficients of four PAHs spiked simultaneously at low concentration (10 µg/L). The only deviations from the protocol described above were (i) the use of multiple deuterated PAH internal standard and (ii) the GC oven program (holding at 55 °C for 1 min, then ramped 10 °C/min to 320 °C, which was held for 25 min).

The sorbed PAH concentrations on nC60 for single and multiple solute experiments were calculated by mass balance from the measured PAH concentrations on POM (SI Table S2).

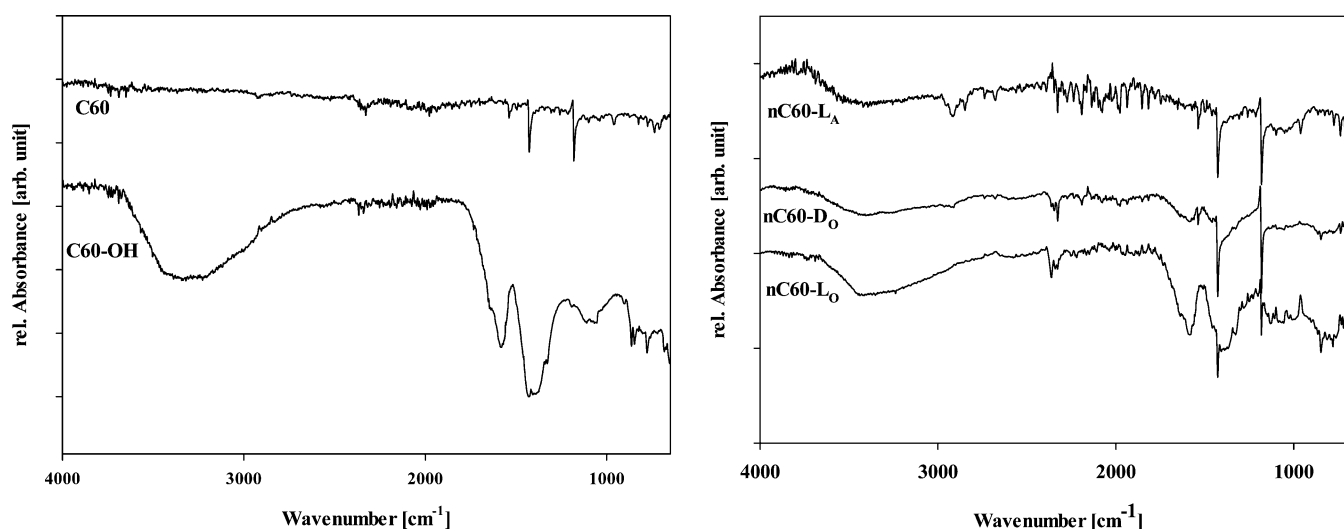


Figure 1. ATR-FT-IR spectra of bulk sorbent material (left) and C60 dispersions after different pretreatments (right).

Sorbent Characterization. For each pretreatment, the particle size distribution in the whole dispersion was determined using a particle and shape analyzer based on laser light shading (time of transition principle, TOT) and simultaneous microscopy (EyeTech, Ankersmid Lab, Nijverdal, The Netherlands). TOT uses laser obscuration time on the detector and a pulse-length analysis to determine particle size and diameter distribution (with a 95% number based confidence level).¹⁷ The hydrodynamic diameter, polydispersity index (Pdl), and zeta potential (ZP) of the particles remaining in dispersion after 4 days of sedimentation were determined by dynamic light scattering (DLS) using a Zetasizer Nano-ZS (Malvern Instruments Ltd., UK) and a refractive index of 2.2 for fullerenes.¹⁸

Surface functionalization was determined by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; System 2000 FT-IR, Perkin-Elmer) and X-ray photoelectron spectroscopy (XPS; Hemispherical energy analyzer PHOISBOS 100 and high-intensity twin anode X-ray source XR-50, SPECS, Berlin, Germany). Bulk and polyhydroxy fullerenes were analyzed as received whereas samples of dispersions were dried for 2 days at 80 °C prior to analysis.

Sorption Models and Statistics. Three sorption models commonly used for CNTs^{19,20} and nC60^{7,20} were fit to the sorption isotherms (model equations and their fitting parameters are listed in SI Table S3). Briefly, the Freundlich model (FM) is an empirical relationship that well describes sorbents with heterogeneous distribution of energy of available sorption sites. The Langmuir model (LM) assumes an even distribution of sorption site energies with the formation of a sorbate monolayer until saturation. The Dubinin–Ashtakov model (DAM) is based on the Polanyi potential theory, in which the sorption potential of a sorbate in a sorption space at the sorbent surface is assumed to depend on the distance between sorbate and sorbent surface (for a detailed description of isotherm models refer to Allen-King et al.²¹). Three additional models were tested: the dual Langmuir model, considering high- and low-energy sorption sites, and two dual mode models based on FM and LM. The latter two models combine linear partitioning and specific sorption modes. However, none of these additional models significantly improved the goodness of fit (data not shown). In fact, the

parts of the dual mode models representing partitioning were negligibly small and the model specific sorption coefficients were identical to those derived from single mode models. FM, LM, and DAM showed the best fits; hence, these three models were considered for the discussion below.

Curve fit was evaluated on a 3-fold criteria basis including the coefficient of determination (R^2), the mean weighted square error (MWSE), and Akaike's Information Criterion (AIC). R^2 , calculated from the sum of the squares of the residuals, does not take into account the number of fitting parameters; hence, MWSE was additionally considered to account for potential overparameterization. AIC is based on information theory. Probability and evidence ratio were calculated to compare model fits of nC60 dispersions (as in detail described in ref 22). All statistical tests and model fits were performed with Sigma Plot 12.0 for Windows. Standard errors of model parameters were computed with reduced Chi-square and weighted regression with weighting to reciprocal y^2 .

RESULTS AND DISCUSSION

Sorbent Characterization. The degree of surface oxidation was assessed for bulk materials of C60 and C60-OH and dried samples of nC60 dispersions by FT-IR (Figure 1). Intensive peaks at 1427 and 1181 cm^{-1} were observed for bulk C60, which can be assigned to C–C vibrational modes of the C60 molecule.²³ Spectra of bulk C60-OH revealed characteristic peaks for –OH, C–O, and C–OH stretching at wavenumbers of 3319, 1068, and 1408 cm^{-1} , respectively. None of these bands were obtained for bulk C60. Both spectra are consistent with previously reported data for these materials.¹⁶ The spectra of both anoxic dispersions were almost identical (hence only that of nC60-L_A is given in Figure 1), showing peaks at C–C vibrations similar to the parent C60. Additionally, a broad band at 3400 cm^{-1} was obtained indicating the presence of remaining water despite drying. The spectra of oxic dispersions showed characteristic peaks also obtained for C60 and C60-OH implying that oxidation occurred at the outer surface of the C60 clusters, whereas no oxidation occurred in the core of the particles.¹⁶ Additionally, XPS spectra of the O(1s) region of the samples C60, nC60-D_O, and nC60-L_O (SI Figure S2) supported the results of FT-IR that sorbent materials kept under oxic conditions showed an

Table 1. Main Characteristics of the Sorbents^a

| sample | Z_{ave} [nm] ^b | PdI ^b | peak [nm] ^b | ZP [mV] ^b | D [1,0] ^c [μm] |
|---------------------|-----------------------------|------------------|---|----------------------|---------------------------|
| nC60-OH | 218 ± 54 | 0.373 | peak 1 = 216.17 ± 29.30 (peak 2 = 54.03 ± 18.51) | −48.00 ± 2.43 | n.d. |
| nC60-L _O | 332 ± 35 | 0.328 | 297.76 ± 32.04 | −51.60 ± 0.60 | 1.16 ± 0.02 |
| nC60-D _O | 439 ± 47 | 0.449 | 350.08 ± 55.35 | −52.13 ± 0.40 | 1.43 ± 0.05 |
| nC60-L _A | 281 ± 8 | 0.215 | 294.22 ± 14.55 | −33.57 ± 1.15 | 1.09 ± 0.02 |
| nC60-D _A | 295 ± 48 | 0.203 | 303.27 ± 28.31 | −30.50 ± 0.26 | 1.02 ± 0.01 |
| nC60 | (3096 ± 771) | 0.860 | 540.12 ± 111.18 | −11.63 ± 2.32 | 4.18 ± 0.26 |

^a ± standard errors ($n = 5$); n.d.: not detectable; pH 6.52 ± 0.36 . ^b hydrodynamic diameter (Z_{ave}), polydispersity index (PdI), intensity-weighted mean (Peak), and zeta potential (ZP) determined by DLS. ^c The number-based diameter of sorbent particles (D[1,0]) was measured by TOT.

increase in surface oxidation. XPS spectra of the C(1s) region of these samples confirm previous data indicating a shift in binding energy with increasing carbon oxidation (data not shown).⁹ Overall, FT-IR and XPS data indicated that significant oxidation occurred for the samples kept in oxic conditions (especially when combined to lamp light exposure, nC60-L_O).

It has been proposed that extended exposure of C60 to water resulted in the introduction of oxygen-containing surface functional groups, whose density on the sorbent surface was not large enough to be detected by titration or elemental analysis.²⁴ The addition of H₂O to C=C bonds in the aromatic molecule of C60 was excluded by Labille et al.²³ and the rate of C60 transformation was greatly reduced in the absence of oxygen.⁹ FT-IR data of the present study showed that oxidation of C60 in anoxic dispersions was minimal. However, oxidation of these sorbents cannot be fully excluded as the mechanisms of hydroxylation of nC60 and lamp light-assisted nC60 dispersion are not yet fully understood. Nevertheless, our findings are consistent with literature data.^{15,16}

The zeta potential (ZP) of nC60 particles in all dispersion scenarios were significantly more negative ($p < 0.001$) than that of initially dispersed C60 (nC60, Table 1). It should be noted that ZP of nC60 suggests that particles in that dispersion are unstable and thus tend to aggregate. Furthermore, ZP of C60 particles in oxic dispersions was significantly smaller ($p < 0.001$) than that of anoxic C60 dispersions. Ionic strength and pH have been previously shown to influence ZP of aqueous nC60 dispersions.^{24–26} However, the changes in ZP observed here among dispersion scenarios can be assigned to changes in surface properties of sorbents, as both ionic strength and pH in all nC60 dispersions were identical (pH 6.52 ± 0.36).

The effect of surface functional oxygen groups on the sorption of hydrophobic organic compounds (HOC) has been previously studied for MWCNTs. A linear and negative relationship between the oxygen content of MWCNTs and maximum sorption capacity was observed. A concentration of oxygen of 10% resulted in a 70% decrease in sorption capacity for naphthalene.²⁷ Similarly, sorption capacities of MWCNTs for benzene, toluene, and *m*-xylene were significantly reduced by an oxygen content larger than 4.7%.²⁸ The FT-IR and ZP data support a similar trend in the present study as discussed in the next section.

Single Solute Pyrene. Sorption of pyrene generally decreased in the following order: nC60-D_A = nC60-L_A > nC60-D_O > nC60-L_O > nC60-OH (Figure 2). Sorption isotherms could be grouped into three categories of decreasing sorption potential: category I > category II > category III. Category I included both sets of samples maintained under anoxic conditions (nC60-L_A and nC60-D_A), for which oxidation processes of sorbent material were minimized. The

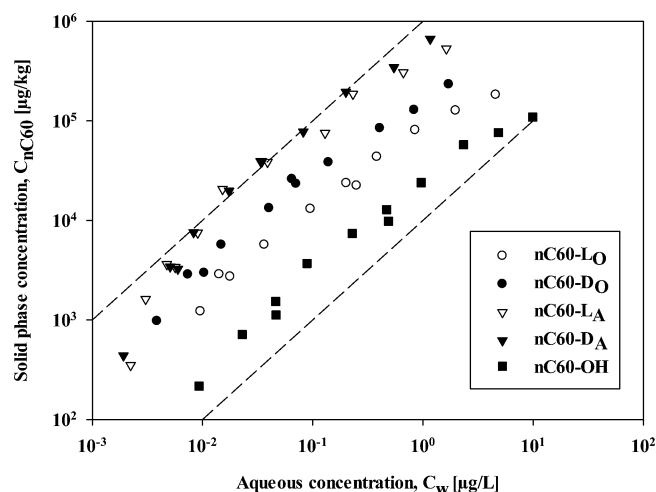


Figure 2. Sorption isotherms of single solute pyrene experiments. Dashed lines show linear sorption ($n = 1$), drawn for visual aid.

data suggest that exposure to lamp light in the absence of oxygen had no influence on surface properties nor on sorption of pyrene (as further discussed below). Category II comprised both nC60 dispersions exposed to oxygen (i.e., nC60-D_O and nC60-L_O), for which exposure to lamp light further decreased sorption of pyrene. Category III consisted of commercial polyhydroxy fullerenes (nC60-OH) with an average number of surface −OH groups of 18–22 per C60 molecule (given by the supplier), for which the smallest sorption was observed. The effects of particle size and change in surface chemistry of the sorbents on their sorption of pyrene are further discussed below.

Effect of Sorbent Properties on Sorption. Table 1 presents the characteristics of the sorbents determined by DLS and TOT. Generally, all C60 dispersions were heterodispersed having a rather large polydispersity index (PdI) of about 0.21–0.45 (Table 1). The PdI decreased for all five C60 dispersion scenarios relative to the initially dispersed bulk material (nC60 in Table 1) as a result of shaking.²⁹ Interestingly, oxic dispersions had larger PdI and particle sizes measured by DLS than those shaken under anoxic conditions. This was in contradiction to the expected as a change in surface chemistry due to presence of oxygen containing functionalities would lead to a decrease in both hydrophobicity and particle size.¹⁰ However, it cannot be excluded that the smaller PdI of particles in anoxic dispersions was rather related to a small size distribution of aggregates.

All pretreatments significantly decreased the particle size ($p < 0.001$) relative to the initial dispersion. Particle sizes of the two anoxic nC60 dispersions were identical ($p > 0.05$). Conversely,

Table 2. Coefficient of Determination (R^2), Mean Weighted Squared Error (MWSE), and Akaike's Information Criterion (AIC) Determined for Three Models Fitting the Sorption Isotherms of Pyrene by Different Dispersion Scenarios of nC60^a

| sample | Freundlich model (FM) | | | Langmuir model (LM) | | | Dubinin–Ashthakov model (DAM) | | |
|---------------------|-----------------------|--------|--------|---------------------|--------|--------|-------------------------------|--------|--------|
| | R^2 | MWSE | AIC | R^2 | MWSE | AIC | R^2 | MWSE | AIC |
| nC60-L _O | 0.93 | 0.0538 | −24.92 | 0.96 | 0.0299 | −31.38 | 0.97 | 0.0256 | −29.16 |
| nC60-D _O | 0.92 | 0.0668 | −22.54 | 0.97 | 0.0293 | −31.59 | 0.98 | 0.0175 | −33.33 |
| nC60-L _A | 0.61 | 0.3878 | −4.55 | 0.56 | 0.4383 | −3.09 | 0.95 | 0.1201 | −15.23 |
| nC60-D _A | 0.76 | 0.2443 | −8.28 | 0.66 | 0.3454 | −4.47 | 0.98 | 0.0270 | −28.58 |
| nC60-OH | 0.92 | 0.0767 | −24.82 | 0.96 | 0.0440 | −31.48 | 0.97 | 0.0357 | −31.79 |

^aDetails of curve fit results and quality criteria are given in SI Table S4.

lamp light exposure resulted in a significant decrease in particle size for the oxalic pretreatment ($p \leq 0.001$). It is known that the large clusters initially formed by C60 in aqueous dispersions can be broken down by extensive mixing.¹⁸ Gai et al.⁷ recently reported smaller C60 particle sizes than those observed in the present study. Considering that Gai et al. kept the dispersions in the dark and under oxalic conditions for no longer than 4 weeks, discrepancies with our results can be assigned to differences in the shaking protocol (i.e., magnetic stirring versus horizontal shaking).³⁰

Among all samples, nC60-D_A and nC60-L_A had the smallest number-based diameter measured by TOT ($D[1,0]$ of 1.02 and 1.09 μm , respectively, Table 1). Therefore, more sorption sites may be available at the particle surface of nC60-D_A and nC60-L_A. In fact these dispersions showed the strongest pyrene sorption affinity (Figure 2). Although dispersing fullerene systems was previously observed to result in a stronger sorption potential,^{7,31} the relationship between particle size and sorption was not consistent. A similar phenomenon was observed in the present study as plotting particle sizes and sorption showed no relationship (not shown): nC60-OH had the smallest particle size but also exhibited the smallest pyrene sorption. This can be further confirmed by comparing the orders of decreasing sorption from Figure 2 (i.e., nC60-D_A = nC60-L_A > nC60-D_O > nC60-L_O > nC60-OH) with the order of increasing particle sizes (i.e., nC60-OH < nC60-D_A ≤ nC60-L_A < nC60-L_O < nC60-D_O). Consequently, additional factors aside from sorbent particle size play a major role governing sorption and are thus required to explain discrepancies in sorption behavior.

Sorption Isotherm Fit. All isotherms were nonlinear; hence, commonly used nonlinear isotherm models (i.e., FM, LM, and DAM) were fit to the data obtained for pyrene sorption by five different nC60 dispersions.

DAM provided the best fits for all nC60 dispersions investigated with the largest R^2 (≥ 0.95), smallest MWSE, and AIC (Table 2 and SI Table S4). DAM is based on the Polanyi–Manes theory, which was previously shown to adequately describe the sorption of various sorbates by nC60 and other CNM (for a detailed review, see Pan and Xing³²). The presence of oxygen-containing groups at the surface allows the formation of hydrogen bonds with surrounding water molecules.³³ Since the water molecules need to be replaced by pyrene, sorption is less favorable. Comparing the capacities for pyrene sorption by nC60 dispersions obtained from DAM fit (Q_{max} as displayed in SI Table S4), there was a significant decrease following the order nC60-D_A = nC60-L_A > nC60-D_O = nC60-L_O > nC60-OH ($p \leq 0.01$).

The goodness of fit for sorbents under oxalic conditions only slightly increased from two- to three-parameter models (i.e., from FM or LM to DAM); therefore, a potential increase in goodness of fit due to overparameterization was investigated by

calculating AIC (probabilities and evidence ratios are given in SI Table S5). For anoxic samples, results clearly indicate that the best fit observed by DAM was not due to overparameterization. This suggests that pore-filling and sorption to flat surfaces are likely the major sorption processes for these sorbents.³⁴ Both hydrophobic C60 particles and hydrophilic polyhydroxy fullerenes form amorphous, loosely associated aggregates in water independent from the degree of hydroxylation.³⁵ These aggregates would thus allow sorbates to sorb into sorbent pores, which has previously been proposed to be a major sorption mechanism for nC60,³¹ unless pore-filling is not hindered by steric³⁶ or other effects.

The goodness of fit of the used sorption models varied among dispersion scenarios. In fact, sorption by oxalic nC60 dispersions was smaller than that by anoxic nC60, and LM gave equal or better fits relative to DAM for oxalic nC60 (SI Table S4). This suggests that for oxalic nC60 a reduced maximum potential sorption space of these sorbents³⁴ and thus potential surface saturation should be taken into account as both models (i.e., LM and DAM) include fitting parameters for maximum sorption capacity (Q_{max}). Additionally, functional groups may reduce the accessibility of sorption sites on the surface of sorbent particles.³² As a consequence, an increased competition between potential sorbates for sorption sites (as further discussed in the next section)³⁷ and/or the formation of three-dimensional clusters that additionally block sorption sites nearby³⁸ have to be taken into account influencing the sorption behavior of nC60. Both processes may contribute to the decrease in sorption observed. By comparing the isotherms of sorbents under oxalic and anoxic conditions together with the data from sorbent characterization, the change in sorption can be related to a change in surface properties resulting from functionalization. Surface hydroxyl groups, on both the commercial polyhydroxy fullerenes and lamp light pretreated sorbent material, may lead to a disruption of the delocalized electron system and, hence, to a decreased sorbate–sorbent interaction (i.e., to a decrease in sorption), which is consistent with the observed isotherms (Figure 2). The results suggest that alterations of nC60 due to the presence of oxygen and irradiation lead to overall decrease in sorption. However, the effect of this change in sorption behavior of nC60 on potential cotransport of other, i.e., ionizable, compounds was not in the focus of the present study but demands further research.

Multiple Solute PAHs. Environmental contaminants typically occur simultaneously, which raises the question of altered sorption due to competition for sorption sites. Competition phenomena are known to be concentration dependent.^{19,39} Sorption experiments with four PAHs were conducted at aqueous equilibrium concentrations in the ng/L range as PAHs are likely to occur at these concentrations in the environment.⁴⁰ Single-point distribution coefficients (log

K_{nC60}) of pyrene were obtained from multiple sorbate experiments, and were compared with single solute $\log K_{nC60}$ values derived from DAM fit results for the corresponding aqueous concentration (SI Table S6). Single and multiple pyrene sorption coefficients were statistically not different for all studied nC60 dispersions. This indicated that no competition for sorption sites among PAHs occurred at the investigated concentration range. The theoretical surface saturation of PAHs on the sorbent (calculated from sorbed concentrations with sorbate molecular area and sorbent surface area of $7.2 \text{ m}^2/\text{g}^{41}$ assuming flat surface sorption) ranged between 2 and 4%; thus, sorption competition as a result of oversaturation of the sorbent surface was unlikely to occur. Strong competition for sorption by MWCNTs was previously observed among naphthalene, phenanthrene, and pyrene coexisting at relatively large concentrations.³⁹ In contrast, sorption coefficients measured for phenanthrene and pyrene in single and multiple sorbate systems together with 11 other PAHs showed no significant competition in the ng/L range.¹⁹

Sorption of a number of low-molecular weight PAHs by nC60 dispersions has previously been reported.^{8,20,31} However, the influence of sorbate properties on the sorption affinity was only briefly discussed. To probe the importance of hydrophobic interactions, the obtained distribution coefficients for five nC60 dispersions were correlated with hydrophobic properties of sorbates (i.e., octanol–water distribution coefficients ($\log K_{ow}$), molar volume (MV), and subcooled liquid solubility ($\log S_i$), as given in SI Table S1). The determined $\log K_{nC60}$ values could be significantly correlated ($p < 0.05$) with $\log K_{ow}$ (SI Table S7a), which suggests that hydrophobic interactions are of major importance for the studied sorbent–sorbate systems. For clarity, it has to be stressed that correlations between distribution coefficients ($\log K_d$) and $\log K_{ow}$ in some cases have to be considered with caution as $\log K_{ow}$ refers to partitioning of a solute between two bulk phases (i.e., absorption), whereas the distribution of a sorbate to CNM is commonly considered as an adsorption process onto its surface. Nevertheless, $\log K_{ow}$ remains the most consulted hydrophobicity parameter in literature for the interpretation of sorption data. Thus, relationships between $\log K_{nC60}$ and $\log K_{ow}$ were investigated to compare sorption by sorbents used in the present study with previously reported results for similar sorbents. The slopes of $\log K_{nC60}$ – K_{ow} relationships in Figure 3 differed from those obtained for other CNM. Generally, the $\log K_d$ – $\log K_{ow}$ slopes are close to 1 for soils and sediments⁴² similar to those in the present study, while slopes for MWCNTs¹⁹ and charcoal⁴³ were much smaller (e.g., 0.3 for MWCNTs). From this it could be said that once aged nC60 does not seem to behave like other carbonaceous materials but rather ordinary geosorbents. Correlations between $\log K_{nC60}$ and hydrophobic properties of sorbates are a first step toward the prediction of sorption of PAHs by nC60.

Although, BaP is much more hydrophobic than BaA, the distribution coefficients for BaP were only slightly larger for anoxic dispersions than those of BaA ($\log K_{ow}$ in SI Table S1). The difference between $\log K_{nC60}$ of BaP and BaA decreased for oxic dispersions, and for nC60-OH $\log K_{nC60}$ of BaP was even smaller than that of BaA. This suggests that (i) for oxic C60 dispersions the contribution of hydrophobic interactions decreases, although they probably still dominate, and/or (ii) pores in these nC60 aggregates are too small for larger sorbates as discussed above. Hydrophobic interactions have been used to interpret sorption between HOC and CNM, even though

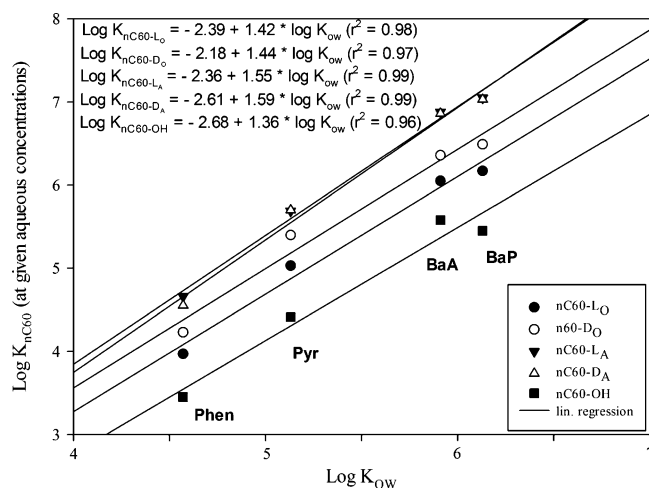


Figure 3. Relationships between single-point distribution coefficient ($\log K_{nC60}$) and $\log K_{ow}$ (from 42) of PAHs in C60 dispersions.

interpretation of sorption data on hydrophobic interactions alone was not sufficient.⁴⁴ A number of mechanisms may contribute to the overall sorption to carbon nanotubes (e.g., van der Waals and electron donor–acceptor (EDA) interactions).³² Similar interactions are expected to play an important role in the dispersion systems presented here. In addition, hydrogen bonding may contribute to sorption when oxygen containing functional groups are present at the sorbent surface.³² Based on solute descriptors used in poly parameter linear free energy relationships (ppLFER), PAHs may only act as hydrogen-bonding acceptors (i.e., hydrogen bonding acidity = 0 but basicity >0 ;⁴⁵ a detailed description of ppLFER can be found in literature, e.g., ref 46). The presence of $-\text{OH}$ and $-\text{COOH}$ groups on CNM surface makes the sorbent possible hydrogen-bonding donors,^{44,47} emphasizing the possible contribution of hydrogen bonding.

Hydrophobicity normalized distribution coefficients (i.e., K_{nC60}/K_{ow} ratio) have previously been used as a tool to estimate the fraction of overall sorption that is not due to hydrophobic interaction.^{19,36} Hence, K_{nC60}/K_{ow} was related to polarizability and hydrogen bond basicity (B) of PAHs (as displayed in SI Table S1) in order to evaluate a possible contribution of hydrogen donor–acceptor interactions (results shown in SI Table S7b). However, a significant correlation could not be observed; neither between K_{nC60}/K_{ow} and polarizability nor B . Thus, considering hydrogen bonds for the interpretation of relevant molecular interactions could not help interpreting the observed differences in $\log K_{nC60}/K_{ow}$ relationships for sorption of PAHs by the studied C60 systems. Endo et al. used ppLFER to identify the most significant type of specific interactions by subtracting ppLFER terms for non-specific interactions from determined distribution coefficients.⁴⁸ However, phase descriptors are not yet available for nC60. Sorption data for a much broader set of probe compounds, covering various chemical classes, are thus necessary to further investigate the contribution of individual molecular interactions to overall sorption (e.g., by ppLFER).

Overall, the findings suggest that molecular interactions with PAHs are independent from the presence of oxygen-containing functional groups on C60 surface. Therefore, hydrogen bonds seem to play a negligible role on sorption behavior of nC60. The presented data set provides a set of scenarios of how aging may affect sorption of dispersed fullerenes in the environment.

Changes in surface chemistry led to significant decrease in both sorption capacity, i.e., amount of sorbate to be sorbed by the sorbent, and sorption affinity, i.e., strength of sorption, for nonionic hydrophobic contaminants. Thus, our results suggest that aging of fullerenes leads to a reduced sorption affinity and capacity, at least for nonpolar contaminants.

■ ASSOCIATED CONTENT

■ Supporting Information

Sorbate properties, isotherm fits, fitting parameters for the models evaluated, and C60 characterization (microscope images and XPS spectra). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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