The Role of Attached Phase Soil and Sediment Organic Matter Physicochemical Properties on Fullerene (nC₆₀) Attachment

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Abstract

Attached phase soil and sediment organic matter is ubiquitous in the sub-surface environment, with a tendency to strongly sorb contaminants, and therefore it may play an important role in contaminant transport. In this study, the deposition of C₆₀ nanoparticles onto attached phase Harpeth Humic Acid and Harpeth Fulvic Acid (HHA and HFA) is explored by using a quartz crystal microbalance with dissipation monitoring and systematically varying thermal energy. By comparing the C₆₀ attachment onto HHA and HFA surfaces to that of bare silica and DLVO predictions, we find that the HHA and HFA layers hinder attachment at low temperatures, while HHA enhances attachment at higher temperatures. Based on thermal characterization of the HHA and HFA layers compared to the corresponding attachment trends, the attachment efficiency is strongly correlated with hydration of the layer. Possible mechanisms explaining this phenomenon include water-

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assisted disruption of polar SOM contacts and hydration-induced swelling of the AP-SOM matrix. Since humic substances typically dominate subsurface organic matter, these results may prove crucial to understanding the complex interactions of engineered nanomaterials in both the natural and engineered environment.

Keywords: fullerene, "C60", humic acid, fulvic acid, QCM-D, SOM

1. Introduction

In 2014, the nanotechnology market was valued at around \$26 billion and it is expected to grow to \$64.2 billion over the next five years (McWilliams, 2014). In particular, the buckminsterfullerene (C_{60}) molecule has attracted much attention due to its widespread applications in many areas (e.g. biomedical technology, electronics, and optics) (Mauter and Elimelech, 2008; Bosi et al., 2003; Nel et al., 2006). With such a high level of production and dissemination, the eventual release of C_{60} into the environment is inevitable, either from industrial sources or through disposal in municipal waste. Several studies have investigated and revealed the potential human health effects, aquatic toxicity, and antimicrobial properties of C_{60} (Nel et al., 2006; Kamat et al., 2000; Lyon et al., 2006; Nakajima et al., 1996). The ongoing environmental release coupled with a strong potential for toxicity raise serious concern for the fate and transport of this material in the environment.

The fate and transport of C_{60} is mainly influenced by aggregation and deposition processes, which are controlled by a complex balance of variables including pH, ionic strength, and presence of organic matter (Lin et al., 2010). Once in the environment, C_{60} will interact with natural soils and sediments,

19 and thus, organic matter attached on the soil and sediment surfaces. At-
20 tached phase soil and sediment organic matter (AP-SOM) is the product of
21 on-site physical and biological decomposition and is an essential component
22 of natural soils and sediments. AP-SOM has been found to strongly sorb
23 hydrophobic organic chemicals (HOCs) and thus influence their transport
24 (Weber et al., 2001). If similar interactions between AP-SOM and C₆₀ ex-
25 ist, these interactions will influence potential pathways of exposure and their
26 eventual impact on ecosystems and human health.

27 Humic substances, including humins, humic acids, and fulvic acids, typ-
28 ically represent the dominant organic components in soils and sediments
29 (Stevenson, 1994). Chemically, humic substances are a mixture of both
30 substituted aromatic and aliphatic compounds, forming a complex physical
31 structure held together by inter- and intra-molecular interactions (Sutton and
32 Sposito, 2005) and therefore represent complex mixtures of macromolecules
33 with varying degrees of crosslinkages. An important factor when considering
34 the macromolecular properties of SOM is, of course, the presence of water.
35 The hydration of SOM has been shown to alter the SOM matrix in several
36 key ways, namely through altered physicochemical properties. Water has
37 been shown to interact strongly with hydrophilic SOM, including fulvic and
38 humic acids, resulting in water uptake and swelling of the macromolecular
39 matrix (LeBoeuf and Weber, 1997; LeBoeuf, 1998). The physicochemical
40 changes in SOM due to increased hydration have also been shown to signifi-
41 cantly increase the sorption of HOCs (Graber and Borisover, 1998; Borisover
42 et al., 2001; Borisover and Graber, 2002; Graber et al., 2007). The mech-
43 anism for increased sorption of HOCs due to increased hydration is likely

44 explained by water-assisted disruption of polar SOM contacts, as described
45 by Graber and Borisover (1998). As hydration increases, water molecules
46 penetrate the SOM matrix and reach polar areas that were previously un-
47 available to HOC interaction, due to inter- or intra-molecular interactions.
48 By hydrating these areas, the water molecules disrupt the interactions be-
49 tween these contacts and provide a new sorption site, which was previously
50 unavailable. The extent to which this sorption enhancing characteristic of
51 SOM hydration may apply to the deposition behavior of C_{60} , however, has
52 not yet been investigated.

53 Dissolved organic matter (DOM), in the form of humic substances, has
54 been shown to adsorb to the surface of C_{60} aggregates and, through steric
55 repulsion, increase their stability to aggregation (Chen and Elimelech, 2007)
56 and deposition (Chen and Elimelech, 2008). Until very recently, however,
57 little work has been done to investigate the interaction between C_{60} and
58 the other form of ubiquitous SOM, AP-SOM. In recent studies, AP-SOM
59 has been shown to enhance, hinder, or have no effect on the attachment of
60 C_{60} depending on the type of AP-SOM and the ionic strength of solution
61 (Chen and Elimelech, 2008; Qu et al., 2012). Furthermore, depending on
62 the stabilizer, the transport of carbon nanotubes through humic acid coated
63 quartz sand grains has been shown to vary between complete retention and
64 minimal retention (Lu et al., 2014). Due to the variable nature of conclusions
65 presented in these studies, it is clear that AP-SOM will play a complex role
66 in the deposition of C_{60} , likely dependent upon the type and physicochemical
67 properties of AP-SOM and the ionic strength of solution.

68 The purpose of this study is to further investigate the role AP-SOM plays

on the deposition of C_{60} by varying the type and physicochemical properties of AP-SOM. Using a quartz crystal microbalance with dissipation monitoring (QCM-D), the deposition of C_{60} onto silica surfaces with and without coatings of humic and fulvic acid was studied, while altering the physicochemical properties of the layer by varying temperature. The attachment efficiencies of C_{60} onto three different surfaces as a function of temperature are then compared to DLVO theory predictions, and the effect of AP-SOM physicochemical properties on the transport of C_{60} is discussed. Not only will knowledge of AP-SOM and engineered nanomaterial (ENM) interactions improve the understanding of the fate and transport of ENMs in the natural environment, but it will also aid in the engineered environment, through improved understanding of factors influencing the deposition behavior of similar types of ENMs for applications in water and wastewater treatment.

2. Materials and Methods

2.1. Materials and solution chemistry

Sublimed C_{60} powder (99.9%) was purchased from MER Corporation (Tucson, AZ). Dry Harpeth River Humic Acid (HHA) and Fulvic Acid (HFA) were isolated as described in our previous publication (DeLapp et al., 2005). Sodium phosphate monobasic (S5011), sodium phosphate dibasic (S5136), and poly-L-lysine hydrobromide (PLL, P1274) were purchased from Sigma-Aldrich (St. Louis, MO). Reagent grade NaCl (S671) was purchased from Fisher Scientific (Pittsburgh, PA). Silica-coated QCM-D sensors (QSX-303) were purchased from Q-Sense (Biolin Scientific, Stockholm, Sweden). All solutions were prepared using ultra pure water purified by the Milli-Q Water

93 Purification system from Millipore (Billerica, MA).

94 Sodium phosphate monobasic and sodium phosphate dibasic were mixed
95 on a 50% molar basis to produce a phosphate buffer that would maintain
96 all solutions at a pH of 6.7 ± 0.1 . The background electrolyte concentration
97 for all experiments consisted of 70 mM NaCl and 2 mM of the previously
98 described phosphate buffer.

99 2.2. C_{60} stock suspension and SOM Stock Solutions

100 The C_{60} stock suspension was prepared using a method described by
101 Andrievsky et al. (1995) (details of the preparation method are provided in
102 Appendix A.1). The resulting C_{60} stock suspension was determined to have
103 a total carbon content (Shimadzu TOC-V CPH/CPN, Columbia, MD) of
104 30.48 mg/L and an unadjusted pH of 5.5. The suspension was stored in the
105 dark at 4 °C for the entirety of the study. All experiments took place within 3
106 months of preparing the C_{60} stock suspension, during which time the particle
107 size was stable, as confirmed by periodic Dynamic Light Scattering (DLS)
108 monitoring (Malvern Zetasizer Nano ZS, Worcestershire, UK).

109 The method for preparing the HHA and HFA solutions, used to build the
110 AP-SOM layers, are provided in Appendix A.2. Using DLS, the intensity
111 weighted hydrodynamic diameter of the HHA and HFA particles in solution
112 was determined to be 247 and 390 nm, respectively. Also using DLS, the zeta
113 potential of the HHA and HFA particles were determined to be -43 and -12
114 mV, respectively, based on 14 independent measurements. Both solutions
115 were stored at room temperature in the dark for the entirety of the study,
116 during which time the particle size was stable, as confirmed by periodic
117 DLS monitoring. The HHA and HFA used in this study were characterized

in a previous publication by DeLapp et al. (2005) and the elemental and functional group analysis are provided in Tables B.1 and B.2 (Appendix B.1). Further characterization of the HHA and HFA layers can be found in Appendix B.1.

2.3. C_{60} deposition experiments

The deposition of C_{60} nanoparticles onto silica surfaces with and without HHA and HFA coatings was explored using a Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D, Q-Sense E4 unit, Biolin Scientific, Stockholm, Sweden). The unit consists of 4 flow modules, each containing a 5 MHz AT-cut quartz crystal sensor. Flowrates were 0.1 mL/min, ensuring laminar flow within the flow module. Temperatures of the solution and flow module were maintained at ± 0.02 °C by a Peltier element.

Before each experiment, the silica coated quartz sensors (QSX303) were soaked in a 2 % Hellmanex II solution overnight, rinsed with copious amounts of deionized water, dried with ultrapure N_2 gas, and then cleaned in a UV-Ozone cleaner (Jelight 42 UVO Cleaner, Irvine, CA) for 20 minutes. Immediately after cleaning, the sensors were loaded into the QCM-D for execution of the experiment.

A representative C_{60} deposition experiment protocol is illustrated in Fig. 1, with detailed description provided in Appendix A.3. As C_{60} deposited onto the sensor surface, the mass continually increased, causing a continuous decrease in frequency, as described by the Sauerbrey Relation (Sauerbrey, 1959) (Eq. 1), where m is the mass of material deposited, C is the crystal constant ($17.7\text{ngcm}^{-2}\text{Hz}^{-1}$), and f_n is the frequency at overtone n . The first 120 seconds of frequency drop corresponding with C_{60} deposition were considered

143 in calculating the initial deposition rate at each experimental condition.

$$\Delta m = -C \frac{1}{n} \Delta f_n \quad (1)$$

Figure 1: Representative C_{60} deposition experiment. The initial baseline was collected in the background solution (A) before PLL was attached to the silica surface (B). The attached PLL was then washed in the background solution (C) before HHA was attached to the PLL surface (D). The attached HHA was then washed with background solution and the temperature of the sensor and chamber was lowered to 15 °C (E). Once a stable baseline was observed at the new temperature, the C_{60} nanoparticle suspension with background solution was introduced and attached to the HHA surface (F).

144 While C_{60} deposited onto the sensor surfaces, the first 120 seconds of the
145 shift in the third overtone of frequency (f_3) were used to calculate the initial
146 deposition rates. In order to compare deposition rates at different experimen-
147 tal conditions independent of C_{60} aggregation effects (Chen and Elimelech,
148 2006), the deposition rates were normalized by calculating the attachment
149 efficiency factor (α). The attachment efficiency factor was calculated (Eq.

2) by normalizing the initial deposition rates to the corresponding initial deposition rate under favorable (nonrepulsive) conditions. Here, the favorable deposition rates are provided by the deposition rates of C₆₀ onto oppositely charged PLL layers at identical experimental conditions.

$$\alpha = \frac{df_3/dt}{(df_3/dt)_{fav}} \quad (2)$$

3. Results and Discussion

3.1. C₆₀ nanoparticle suspension

Investigation by Transmission Electron Microscopy (TEM) (Philips CM 20 TEM, Eindhoven, Netherlands) suggested the particles were polydisperse, as seen in Fig. 2, where representative images of an aggregate (left image) and individual particles (right image) are shown. DLS measurements confirmed a polydisperse particle distribution with an intensity weighted hydrodynamic diameter of the C₆₀ nanoparticles of 103 nm based on 14 independent measurements and a zeta potential of -42 mV, based on 20 independent measurements. The zeta potential of the suspension was measured over a pH range of 3–10 and the results remained negative over the entire pH range investigated. Figures B.10 and B.11 (Appendix B.2) summarize particle size distribution and zeta potential measurements.

3.2. C₆₀ attachment analysis

The deposition behavior of C₆₀ onto bare silica has been shown to be in qualitative agreement with DLVO theory (Chen and Elimelech, 2006), therefore the total interaction energy profiles for C₆₀ approaching a bare

Figure 2: Representative TEM images of the C_{60} nanoparticle suspension.

171 silica surface were calculated for each temperature investigated and presented
 172 in Fig. 3. The detailed DLVO calculations are presented in Appendix C.
 173 As temperature increases, the total interaction energy profiles remain very
 174 similar, except for a small decrease in the energy barrier.

175 For the first time, the attachment efficiency factors of C_{60} , onto three
 176 different surfaces, as a function of temperature are presented in Fig. 4. The
 177 bare silica attachment trend appears rather flat, with a small net increase,
 178 though the total increase does not fall outside the error of the measure-
 179 ments. This can be considered relatively consistent with DLVO predictions
 180 (Fig. 3), as the energy barrier shows a small decrease with increasing temper-
 181 ature, which could lead to a negligible increase in attachment. The presence
 182 of HHA and HFA coatings cause significant deviations from the bare silica
 183 trend. Compared to the attachment onto bare silica, both HHA and HFA
 184 hinder C_{60} attachment at lower temperatures, while HHA enhances attach-
 185 ment at higher temperatures. At the highest temperature investigated, HHA

Figure 3: Calculated DLVO interaction energy profiles as C_{60} approaches a bare silica surface.

186 greatly enhances attachment while HFA appears to marginally enhance it,
 187 including a very slight overlap of error bars with the bare silica curve. The
 188 HHA and HFA trends continuously increase with increasing temperatures,
 189 though the rate of increase appears complex, presumably due to the change
 190 in physicochemical properties of the SOM layers over the temperature range
 191 investigated. The HHA trend displays a rate increase throughout the tem-
 192 perature range investigated, while the HFA trend appears to level off and
 193 then recover. The largest increase in attachment for both surfaces occurs
 194 in the temperature range of 35–45 °C. This suggests that the AP-SOM lay-
 195 ers undergo the largest change in physicochemical properties in this region.
 196 Previous studies of the HHA and HFA have illustrated thermal transitions
 197 within this region (DeLapp et al., 2005), however these studies investigated
 198 the materials as a dry, bulk powder. In our current work, the HHA and

Figure 4: C_{60} attachment efficiencies onto bare, HHA-coated, and HFA-coated silica sensors as a function of temperature. Error bars represent the standard deviation.

199 HFA are examined as thin, hydrated layers, bringing into account additional
 200 variables and, because of this, the degree to which these studies apply to the
 201 current work is unknown.

202 3.3. Thermal effects on attachment

203 In order to understand the deviation in attachment onto the HHA and
 204 HFA surfaces, the thermal properties of the SOM layers were investigated
 205 using the QCM-D. This is a particularly novel approach because the QCM-
 206 D has never before been used to thermally characterize AP-SOM. First, each
 207 AP-SOM layer was constructed following the same procedure as executed
 208 for the deposition experiments and as described previously. Then, the layer
 209 was exposed to a temperature ramp covering the entire temperature range of
 210 this study. The density and viscosity of water are a function of temperature,
 211 so the response of the sensor submerged in a solution is also expected to

Figure 5: Thermal characterization of the HHA layer by QCM-D, with all bulk solution and sensor effects subtracted, compared to the corresponding C₆₀ attachment efficiency trend. The 3rd overtone of frequency is displayed.

change as a function of temperature (Ishida and Biggs, 2007). In order to isolate the effects caused only by changes in each AP-SOM layer, the same bare sensor was first taken through an identical temperature ramp and its response was subtracted. In this manner, the QCM-D was utilized to thermally characterize a thin layer of AP-SOM. The frequency curves displayed in Figs. 5 and 6 represent the response of the HHA and HFA layers, respectively, to a change in temperature. By comparing the AP-SOM frequency response to the corresponding C₆₀ attachment trend, we can gain insights into the mechanisms by which the attachment onto each AP-SOM deviates from that of bare silica.

The frequency curve provides insight into the mass changes of the layer, including any water molecules that are hydrating the layer. The overall trend

Figure 6: Thermal characterization of the HFA layer by QCM-D, with all bulk solution and sensor effects subtracted, compared to the corresponding C₆₀ attachment efficiency trend. The 3rd overtone of frequency is displayed.

224 of each frequency curve is downwards, indicating an increase in mass (see Eq.
 225 1), attributable to the hydration of the AP-SOM layer at increasing temper-
 226 atures. The observed increase in hydration with increasing temperature is in
 227 agreement with a study by Vidyasagar et al. (2012), which investigated the
 228 thermal characteristics of a polyelectrolyte using a similar QCM-D method.
 229 As indicated by Figs. 5 and 6, an increase in hydration (decrease in fre-
 230 quency) corresponds with an increase in attachment for both AP-SOM layers
 231 investigated. As the HHA layer begins to hydrate between 15–25 °C, the at-
 232 tachment shows a small increase (Fig. 5). As the HHA continues to hydrate
 233 more rapidly between 25–35 and 35–45 °C, the attachment also results in a
 234 sharper increase. As the HFA layer begins to hydrate in the range of 15–25
 235 °C, the attachment begins to rise as well (Fig. 6). As the HFA hydration

236 rate slows and begins to reverse in the range of 25–35 °C, however, the in-
237 crease in attachment slows and begins to level off. The lack of an observable
238 decrease in attachment in this region suggests that the interaction is a com-
239 plex one, relying on more than just hydration of the layer. As the HFA layer
240 resumes a rapid hydration rate between 35–45 °C, the attachment shows a
241 correspondingly rapid increase. For these reasons, Figs. 5 and 6 clearly il-
242 lustrate a strong correlation between AP-SOM layer hydration and resulting
243 C₆₀ attachment efficiency, which, to our knowledge, has not been illustrated
244 for ENMs.

245 The C₆₀ suspension was also thermally characterized throughout the tem-
246 perature range of 15–55 °C. The particle diameter was found to negligibly
247 increase from 99 nm to 106 nm and the zeta potential showed no discernible
248 change. Summaries of these measurements can be found in Figs. B.12 and
249 B.13 (Appendix B.2), respectively.

250 An increase in hydration of the AP-SOM layers at higher temperatures
251 contribute to the increased attachment behavior through water-assisted dis-
252 ruption of polar SOM contacts, as described by Graber and Borisover (1998).
253 As hydration increases, water molecules penetrate the SOM matrix and
254 reach polar areas that were previously unavailable to C₆₀ attachment, due
255 to inter- or intra-molecular interactions. By hydrating these areas, the wa-
256 ter molecules disrupt the interactions between these contacts and provide a
257 new contact for attachment, which was previously unavailable. This effect
258 has been illustrated for the sorption of HOCs by a Pahokee peat hydrated
259 by water (Graber and Borisover, 1998) and other polar solvents (Borisover
260 et al., 2001). The results of the current study illustrate a similar effect for

261 the attachment of C_{60} by two different humics, bringing into account more
262 complexity in the environmental fate and transport of C_{60} .

263 Another possible contributing factor to the observed increase in attach-
264 ment involves the swelling of the AP-SOM layer. At higher temperatures the
265 AP-SOM layers expand or swell due to increased thermal motions and ap-
266 parent increased hydration, much like the matrix relaxation observed in pre-
267 vious studies (Schaumann, 2005; Schaumann and LeBoeuf, 2005). Swelling
268 will increase the volume of the layers, allowing them to take a more extended
269 conformation from the surface of the sensor and also provide an increasingly
270 cross-linked or bridged mesh of organic matter for the C_{60} particles to become
271 entangled in. At lower temperatures, the AP-SOM layers dehydrate, which
272 compacts the layer. This compacted layer likely has a more condensed, less
273 extended (smoother) surface with reduced potential for C_{60} particle entan-
274 glement, effectively lowering attachment efficiency (Fig. 4). This finding is
275 in agreement with a study by Chen and Elimelech (2008) which investigated
276 the deposition of C_{60} onto an alginate coated silica surface. When the algi-
277 nate was exposed to a higher electrolyte concentration, the layer compacted
278 and resulted in lower attachment efficiency.

279 4. Conclusions

280 In this study, we have shown that the attachment of C_{60} to immobilized
281 layers of HHA and HFA is greatly affected by temperature and that the trend
282 in attachment efficiency onto the AP-SOM layers deviate greatly from that
283 of bare silica. The attachment efficiency onto both AP-SOM layers hinder
284 attachment at low temperatures and then begin to rise as temperatures in-

crease, eventually resulting in enhanced attachment at high temperatures, in the case of the HHA layer. (Fig. 4). Based on thermal characterization of the AP-SOM layers compared to the corresponding attachment trends (Figs. 5 and 6), the attachment efficiency is strongly correlated with hydration of the layer. Regions of rapid hydration correspond to steep increases in attachment and regions of slowed or decreased hydration correspond to lower increases in attachment. Possible mechanisms explaining this phenomenon include water-assisted disruption of polar SOM contacts and hydration induced swelling of the AP-SOM matrix. This thermal effect on the attachment of C₆₀ to AP-SOM may prove to be crucial in understanding the fate and transport of ENMs in areas that are rich in AP-SOM, like the subsurface environment, because humic substances typically represent the dominant organic components in soils and sediments (Stevenson, 1994). In areas that see large temperature fluctuations throughout the year, we may see a much larger uptake of ENMs in the warm seasons and less uptake in the cold seasons. Understanding how ENMs interact with individual components of soil is crucial to understanding the fate and transport of ENMs in a complex soil system, leading to their eventual impact on ecosystem and human health. The thermal effect illustrated in the current study may also prove useful in the removal of similar ENMs from wastewater or drinking water, by exploiting the much higher attachment efficiency at increased temperatures. Further studies need to be carried out, however, to investigate the relative importance of other variables which may play a role in ENM interactions with AP-SOM.

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Appendix A. Details on Experimental Methods

Appendix A.1. C_{60} stock suspension preparation

First, approximately 35 mg of C_{60} powder was dissolved in 30 mL toluene, forming a clear, dark purple solution. Then, 5 mL of this mixture was intro-

417 duced into a beaker containing 50 mL deionized water, forming two distinct
418 phases. This solution was then sonicated (Fisher Sonic Dismembrator 300,
419 Pittsburgh, PA) for more than 3 hours in a fume hood to allow for evapora-
420 tion of the toluene. The beaker was topped off with deionized water every
421 20 minutes to account for the evaporated water. The resulting transparent,
422 brown-yellow liquid was filtered through 0.22 μm pore size membrane filter
423 paper (Fisher, GSWP02500), resulting in a clear, bright yellow liquid. This
424 method was repeated a total of 6 times to produce approximately 330 mL of
425 C_{60} stock suspension.

426 *Appendix A.2. HHA and HFA solution preparation*

427 Fifty milligrams of dry HHA was introduced into 400 mL deionized water
428 and stirred for more than 3 hours. During this time, the pH was adjusted
429 drop wise with 0.1 N NaOH to a pH of 10.0 to allow the HHA to completely
430 dissolve. After 3 hours and complete dissolution of the HHA, the pH was
431 adjusted drop wise with 0.1 N HCl down to a pH of 6.7 and filtered through
432 0.22 μm pore size membrane filter paper. The stock solution was then diluted
433 to 500 mL total volume, including the addition of NaCl and phosphate buffer
434 to make a 0.1 g/L HHA, 70 mM NaCl, and 2 mM phosphate buffer solution.

435 Fifty milligrams of dry HFA was introduced into 400 mL of deionized
436 water and stirred for more than three hours. Once the HFA had completely
437 dissolved, the pH was adjusted drop wise with 0.1 N NaOH to a pH of 6.7
438 and filtered through 0.22 μm pore size membrane filter paper. The stock
439 solution was then diluted to 500 mL total volume, including the addition of
440 NaCl and phosphate buffer, to make a 0.1 g/L HFA, 70 mM NaCl, and 2
441 mM phosphate buffer solution.

442 *Appendix A.3. C₆₀ deposition experimental procedure*

443 The background solution, 70 mM NaCl and 2 mM phosphate buffer, was
444 flowed over the surface of the sensors until a stable baseline was achieved.
445 The signal was considered stable when the third overtone frequency (f_3)
446 failed to drift more than 0.3 Hz over the course of 10 minutes. Once a stable
447 baseline was achieved, 2 mL of a 0.1 g/L PLL solution that contained the
448 same electrolyte and buffer concentrations was flowed across the sensor sur-
449 face. During this time, the PLL adsorbed to the silica surface very rapidly.
450 The PLL layer was then rinsed with 2 mL of the background solution. If
451 PLL is the final layer before C₆₀ deposition, the layer construction ended
452 here. In the case of the HHA and HFA experiments, a solution of 0.1g/L
453 HHA or HFA, containing the same electrolyte and buffer concentrations, was
454 then flowed across the rinsed PLL layer until the signal once again stabi-
455 lized, ≈ 20 minutes. During this time, the oppositely charged HHA or HFA
456 macromolecules readily adsorbed onto the rinsed PLL layer, forming a sec-
457 ond layer. The rapid adsorption of HHA or HFA onto the PLL layer usually
458 resulted in a shift in f_3 of approximately 20 and 22 Hz, respectively. The
459 mass of HHA and HFA deposited onto the sensor surface was calculated to
460 be approximately 411 and 351 ng/cm², respectively, by the Voigt viscoelastic
461 model (Voinova from proposal). A plot of the model calculated masses can
462 be seen in Figure B.7. Finally, the HHA or HFA layer was then rinsed with
463 2 mL of the background solution until a stable baseline was achieved. The
464 layer construction portion of all experiments took place at 25 °C.

465 Once the layers were constructed, the temperature was adjusted to the
466 desired temperature of the C₆₀ deposition experiment. All solutions used

467 in each experiment were held at 2 °C above the set point temperature of
468 the experiment for several hours before the experiment took place to ensure
469 the solutions would not degas on the surface of the sensor. Once a stable
470 baseline was achieved in the background electrolyte, measured amounts of
471 the stock 1 M NaCl and 1 M phosphate buffer were added to the diluted stock
472 C₆₀ suspension to make a C₆₀ concentration of 6 mg/L, with electrolyte and
473 buffer concentrations matching all other solutions. The resulting diluted C₆₀
474 suspension was then immediately flowed into the flow module and across
475 the surface of the sensor. As C₆₀ deposited onto the sensor surface, the mass
476 continuously increased, causing a decrease in frequency (Eq. 1). The first 120
477 seconds of this drop in frequency were used to calculate the initial deposition
478 rates for each set of experimental conditions.

479 **Appendix B. Details on Materials Characterization**

480 *Appendix B.1. Harpeth humic and fulvic acid characterization details*

Table B.1: Elemental analysis and water content of HHA and HFA after DeLapp et al. (2005), reproduced here with permission from the author.

NOM	C (mass %)	H (mass %)	O (mass %)	N (mass %)	S (mass %)	P (mass %)	Water Content (mass %)
Harpeth Humic Acid	51.2	4.9	39.1	4.0	0.56	0.12	5.8
Harpeth Fulvic Acid	43.4	3.4	49.4	1.5	0.20	0.75	5.2

Table B.2: Relative abundance of functional groups by ^{13}C nuclear magnetic resonance (NMR) analysis of HHA and HFA after DeLapp et al. (2005), reproduced here with permission from the author.

NOM	Alkyl 0-50 (ppm)	O-Alkyl 50-112 (ppm)	Aromatic 112-145 (ppm)	Phenolic 145-163 (ppm)	Carboxyl 163-190 (ppm)
Harpeth Humic Acid	0.2	0.28	0.22	0.13	0.18
Harpeth Fulvic Acid	0.15	0.29	0.19	0.18	0.20

481 The mass of the layers formed by depositing HHA and HFA were deter-
 482 mined to be approximately 411 and 351 ng/cm², respectively, by the Voigt
 483 viscoelastic model (Voinova et al., 1999). A plot of the model calculated
 484 masses can be seen in Figure B.7. The AP-SOM layers were further char-
 485 acterized thermally, to ensure that the high temperatures did not facilitate
 486 desorption of the AP-SOM, which would in turn affect C₆₀ deposition. Af-
 487 ter the layers were constructed, as described in Appendix A.3, they were
 488 taken through a temperature ramp which encompassed the entire temper-
 489 ature range of the experiment. Upon cooling the AP-SOM layers, the fre-
 490 quency curve returned to its original value in each case, meaning the mass of
 491 the layers remained unchanged and desorption was not observed. Represen-
 492 tative heating/cooling curves for HHA and HFA can be seen in Figures B.8
 493 and B.9, respectively.

Figure B.7: Calculated mass of the HHA and HFA layers, by the Voigt viscoelastic model.

Figure B.8: The heating/cooling loop of HHA, showing no change in mass over the temperature range investigated.

Figure B.9: The heating/cooling loop of HFA, showing no change in mass over the temperature range investigated.

494 *Appendix B.2. C₆₀ characterization details*

Figure B.10: Particle size distribution of the C₆₀ nanoparticle stock suspension by DLS, based on 14 independent measurements.

Figure B.11: Zeta potential of the C_{60} nanoparticle stock suspension over a pH range of 3–10, by DLS. Each point represents 14 independent measurements and error bars represent a 95% confidence interval.

Figure B.12: Hydrodynamic particle diameter of the C_{60} stock suspensions as a function of temperature. Each point represents 20 independent measurements and error bars represent standard deviation.

Figure B.13: Zeta potential of the C₆₀ stock suspension as a function of temperature. Each point represents 14 independent measurements and error bars represent the standard deviation.

495 Appendix C. DLVO interaction energy calculation details

496 By treating the C₆₀ deposition as a sphere-plate interaction, the total
 497 interaction energy between the C₆₀ particles and the silica sensor surface was
 498 estimated from the sum of the electrical double layer repulsion (V_R) and van
 499 der Waals attraction (V_A). Eq. C.1 (Hogg et al., 1966) was used to calculate
 500 the van der Waals attraction, where A is the combined Hamaker constant
 501 for the C₆₀ water silica system (4.71×10^{-21} J) (Qu et al., 2012), a is the
 502 radius of C₆₀ particles (Table C.3), h is the separation distance between the
 503 C₆₀ particle and silica sensor surface, and λ is the characteristic wavelength
 504 of interaction (usually assumed to be 100 nm) (Jiang et al., 2010).

$$V_A = -\frac{Aa}{6h} \left(1 + \frac{14h}{\lambda}\right)^{-1} \quad (\text{C.1})$$

Eq. C.2 (Hogg et al., 1966) was used to calculate the electrical double layer repulsion, where ϵ_0 is the dielectric permittivity in a vacuum, ϵ_r is the relative dielectric permittivity of water (Table C.3), ζ_p is the zeta potential of the C₆₀ particles (-27.2 mV, remained constant over the temperature range investigated according to DLS measurements), ζ_c is the zeta potential of the silica surface (-30 mV), and κ is the inverse Debye length.

$$V_R = \pi \epsilon_0 \epsilon_r a \left\{ 2 \zeta_p \zeta_c \ln \left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + (\zeta_p^2 + \zeta_c^2) \ln [1 - \exp(-2\kappa h)] \right\} \quad (\text{C.2})$$

Eq. C.3 was used to calculate the inverse Debye length for the electrolyte system (Jiang et al., 2010), where e is the elementary charge, n_j is the number concentration of ions in the bulk solution, z_j is ion valence, k is the Boltzmann constant, and T is the absolute temperature.

$$\kappa = \sqrt{\frac{e^2 \sum n_j z_j^2}{\epsilon_0 \epsilon_r k T}} \quad (\text{C.3})$$

Since the C₆₀ particle radius and relative dielectric permittivity of water vary with temperature, the values used in Eqs. C.1, C.2, and C.3 are summarized in Table C.3. The values for the relative dielectric permittivity of water were obtained from a study by Malmberg and Maryott (1956).

Table C.3: Temperature-dependent C₆₀ particle radius and relative dielectric permittivity of water used to calculate the total interaction energy between the C₆₀ particles and silica sensor surface.

Temperature (°C)	C ₆₀ Particle Radius (nm)	ϵ_r
15	49.7	81.95
25	50.8	78.30
35	52.2	74.83
45	52.5	71.51