

1 **Carbon nanomaterials in clean and contaminated soils: environmental implications and**  
2 **applications**

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6 **Abstract**

7 The exceptional sorptive ability of carbon nanomaterials (CNMs) for hydrophobic organic  
8 contaminants (HOCs) is driven by their characteristically large reactive surface areas and highly  
9 hydrophobic nature. Given these properties, it is possible for CNMs to impact on the persistence,  
10 mobility and bioavailability of contaminants within soils, either favourably through sorption and  
11 sequestration, hence reducing their bioavailability, or unfavourably through increasing  
12 contaminant dispersal. This review considers the complex and dynamic nature of both soil and  
13 CNM physicochemical properties to determine their fate and behaviour, together with their  
14 interaction with contaminants and the soil micro-flora. It is argued that assessment of CNMs  
15 within soil should be conducted on a case-by-case basis, and further work to assess the long-term  
16 stability and toxicity of sorbed contaminants, as well as the toxicity of CNMs themselves is  
17 required before their sorptive abilities can be applied to remedy environmental issues.

18 **Key words:** Carbon nanoparticles; bioavailability; remediation; hydrophobic contaminants; soil

## 19 **1. Introduction**

20 With the continued up scaling of carbon nanomaterial (CNM) production (Nowack and  
21 Bucheli, 2007) as well as the diverse array of consumer (Sharma and Ahuja, 2008), medical (Peretz  
22 and Regev, 2012) and industrial applications in which they are increasingly becoming  
23 incorporated, widespread environmental release of these physically and chemically unique  
24 macromolecules has become inevitable (Köhler et al., 2008). Once released, soils are likely to be a  
25 primary repository (Mueller and Nowack, 2008; Gottschalk et al., 2009), with the quantities  
26 anticipated to increase on an annual basis (Gottschalk et al., 2009). In spite of this, studies  
27 focused on CNMs within soils are scarce, and many areas of uncertainty remain. Understanding  
28 the interactions between CNMs, soils and components therein is therefore an urgent and  
29 essential aspect of any risk assessment process.

30 In their pristine form, CNMs are broadly characterised by their large reactive surface areas,  
31 highly hydrophobic characteristics and high degree of bio-geochemical recalcitrance. They are  
32 known to be toxic to various soil microbiota (Riding et al., 2012a; Riding et al., 2012b), and  
33 possess a high affinity for the sorption of a range of hydrophobic organic compounds (HOCs), such  
34 as polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) (Pan and Xing,  
35 2010). As both PAHs and PCBs are important classes of hydrophobic, toxic organic compounds,  
36 which are both abundant and persistent in soils (Stokes et al., 2005), the potential for CNMs to  
37 modify the availability and mobility of HOCs, either favourably through sorption and  
38 sequestration, or unfavourably through increasing contaminant dispersal, is currently unknown.  
39 Presently, there is only limited and occasionally contradictory information regarding the  
40 implications of contaminants while sorbed to CNMs, as well as the fate and behaviour of CNMs in  
41 uncontaminated soils. Exploring these issues in light of the emerging nature of CNMs as  
42 xenobiotic soil components is therefore essential.

43 This review seeks to answer three key questions. (i) What factors influence the behaviour and  
44 fate of CNMs within the soil environment? (ii) To what extent can CNMs influence the sorption,

45 desorption and mobility of contaminants in soils? (iii) What are the impacts of CNMs on soil  
46 microorganisms and the biodegradation of contaminants in soils?

47

## 48 **2. Carbon nanomaterial diversity and detection**

49 Within the environment, some CNMs can occur naturally or have close naturally occurring  
50 relatives due to various environmental events (Heymann et al., 1994; Chijiwa et al., 1999; Velasco-  
51 Santos et al., 2003; Esquivel and Murr, 2004). However, concentrations occurring naturally are  
52 likely to be relatively small (0.1 to 0.2 parts per million) (Heymann et al., 1994; Chijiwa et al.,  
53 1999). Therefore, when referring to CNMs, this review explicitly focuses on those that are  
54 anthropogenic in origin.

55 The properties of CNMs vary dramatically between the different methods of production,  
56 functionalization status and cleaning/purification methods employed (Nowack and Bucheli, 2007).  
57 Hence, determining their environmental behaviour is all the more challenging, and generalisation  
58 of the characteristics of CNMs is not possible, with each type requiring careful characterisation  
59 (Nowack and Bucheli, 2007). Of the many different forms of CNMs available, this review focuses  
60 specifically on carbon nanotubes (CNTs) and C<sub>60</sub> fullerene, which are two of the most widely  
61 utilised and investigated classes of CNMs (Mueller and Nowack, 2008; Gottschalk et al., 2009;  
62 2010; Petersen and Henry, 2012).

63 To date, CNTs are arguably the most promising of all nanomaterials produced (Giles, 2006). In  
64 their pristine form, CNTs are extremely hydrophobic and consist of graphene sheets rolled into  
65 nanoscale diameter cylinders, the ends of which may contain spherical fullerene cappings (Mauter  
66 and Elimelech, 2008). One single-rolled graphite sheet is called a single-walled carbon nanotube  
67 (SWCNT), while several SWCNTs nested together in a concentric fashion comprise a multi-walled  
68 carbon nanotube (MWCNT) (Pan and Xing, 2008). They consist of sp<sup>2</sup> carbon atom arrangements  
69 in a fused benzene ring configuration, which results in exceptional physicochemical properties  
70 and consequentially their incorporation into a vast array of composite materials (Liu et al., 1999;

71 Snow et al., 2005; Mauter and Elimelech, 2008; Almecija et al., 2009). An excellent and more  
72 detailed discussion about the unique physicochemical properties of CNTs is provided by Mauter  
73 and Elimelech (2008).

74 Fullerenes are spherically arranged carbon atoms resembling a geodesic dome. The size of the  
75 fullerene dome can vary depending on the number and spherical configuration of carbon atoms.  
76 C<sub>60</sub> Fullerene (Buckminster fullerene or Bucky Ball) has arguably the best defined physicochemical  
77 parameters, produced in the largest quantities and has been the focus of most scientific  
78 engagement (Campbell and Rohmund, 2000; Petersen and Henry, 2012). C<sub>60</sub> is comprised of a  
79 spherical configuration of 5- and 6-carbon rings, consisting of 60 carbon atoms in total. It  
80 commonly exists as nano-C<sub>60</sub> (*n*C<sub>60</sub>) particles (regarded as the most environmentally relevant  
81 form), which are crystalline structures containing 100-1000 C<sub>60</sub> molecules (Colvin, 2003; Sayes et  
82 al., 2004). Presently, fullerenes have proposed applications in biology (Lucafò et al., 2012) and  
83 electronic/optical devices as thin films combined with polymers (Richards et al., 2012).

84 Unlike most organic chemicals with well-defined structures, the diversity of particle sizes,  
85 lengths, diameters, charges, surface areas, coatings, molecular weight, impurities and aggregation  
86 states are not necessarily constant. These are often tailored to the intended end-use of the  
87 particles and can be modified by the environmental compartments in which they reside, which  
88 limits their detection and characterisation in soils and other complex environmental matrices  
89 through chromatographic techniques (Petersen et al., 2011). A summary of methods used to  
90 detect CNMs within soils and sediments is presented in Table 1.

91 In addition, as the life cycles of CNM containing products are likely to vary greatly, the means  
92 by which these materials enter the soil environment are also likely to be highly variable (Pan and  
93 Xing, 2012). An excellent review of different CNM exposure scenarios for both humans and the  
94 environment, is provided by Köhler et al. (2008). Further complicating their detection is the  
95 emerging nature of manufactured CNMs as soil xenobiotic components, and hence their presently  
96 low concentrations, together with their interaction with naturally occurring nanomaterials and

97 other environmental components, which leads to particles with sizes and compositions that  
98 significantly differ from their native forms (Nowack and Bucheli, 2007; Darlington et al., 2009;  
99 Chen et al., 2011). As such, careful consideration of multiple environmental variables is required  
100 to determine their impact on CNM fate and behaviour.

101

### 102 **3. CNM behaviour and fate within the soil environment**

103 Once released into the soil, the fate and behaviour of CNMs is governed by their interactions  
104 with various components within the environment. Derjaguin Landau Verwey Overbeek (DLVO)  
105 interactions, such as electrostatic interactions and van der Waals (vdW) forces, and non-DLVO  
106 interactions, such as hydrogen bonding and steric hindrance, ultimately determine the mobility,  
107 aggregation and adhesion of CNMs within soils. These forces may operate in concert to various  
108 extents, with the predominating force controlled by factors such as the properties and quantity of  
109 soil organic matter (SOM), characteristics of inorganic matter, the type and quantity of clays,  
110 together with the properties of CNMs themselves. Each of these factors are heavily influenced by  
111 variables that are not necessarily constant over time, such as pH and ionic strength.

#### 112 *3.1 The impact of soil organic matter*

113 Soil organic matter plays a substantial role in both the fate and behaviour of CNMs through  
114 alterations in the dominance of the various DLVO and non-DLVO interactions. SOM (which  
115 consists primarily of decomposed plant and animal remains (Lee et al., 1981)) is an all-  
116 encompassing term describing organic matter (OM) dispersed ubiquitously throughout the soil  
117 environment, and is composed of a heterogeneous mixture of lipids, carbohydrates, carboxylic  
118 acids, humic substances, hydrophilic acids, proteins, carbohydrates, hydrocarbons and amino  
119 acids. However, the mechanism by which SOM maintains CNMs stability in suspension is still  
120 under investigation and debate (Dinesh et al., 2012). Specifically, the aim of this section is  
121 therefore to provide an overview of recent investigations in which the manner of solid SOM,

122 dissolved organic matter (DOM), humic acid (HA) and tannic acid (TA) influence the behaviour of  
123 CNMs.

124 Adsorption of molecular DOM onto CNMs occurs through either aromatic ring sorption or  
125 binding of aliphatic chains via  $\pi$ - $\pi$  or CH- $\pi$  interactions, leaving the hydrophilic moieties exposed  
126 (Lin and Xing, 2008). Consequentially, the surfaces of CNMs significantly change from a  
127 hydrophobic, aromatic-like structure, to that of the organic, hydrophilic functional groups in DOM  
128 (Zhang et al., 2011a), with potentially large implications for other DLVO and non-DLVO  
129 interactions. In studying  $nC_{60}$ , Kwon (2012), found the type of DOM determined suspension  
130 stability, with those containing long, hydrophobic carbon backbones readily adsorbing via vdW  
131 interactions onto  $nC_{60}$  surfaces, promoting their stability. However, Zhang et al. (2011a) found  
132 peat (diagenetically young SOM) in dissolved form (DOM), also prevented MWCNT aggregation  
133 through both steric hindrance and electrostatic repulsion in sodium concentrations  $>4$  mM or in  
134 solutions of  $pH \geq 4$  (Zhang et al., 2011a). Increasing ionic strength resulted in greater adsorption of  
135 DOM onto MWCNTs (Hyung et al., 2006; Hyung and Kim, 2008; Zhang et al., 2011a) due to  
136 reduced electrostatic repulsion between the DOM and the particle surface. As a result, cations  
137 impairing electrostatic interactions at high ionic strengths in the presence of DOM may slightly  
138 shift the relative importance of suspension mechanisms from electrostatic repulsion, in favour of  
139 steric hindrance (Zhang et al., 2011a); broadly similar results have been identified with  $nC_{60}$  (Qu et  
140 al., 2012). Ionic strength therefore primarily affects the balance between electrostatic repulsion  
141 and steric hindrance mechanisms of particle suspension in the presence of DOM.

142 Typically, frequently occurring cations within the environment ( $K^+$ ,  $Na^+$ ,  $Ca^+$  and  $Mg^{2+}$ ) induce  
143 aggregation and deposition in systems devoid of SOM through reductions in electrostatic  
144 repulsion between particles, hence reducing CNM stability (Zhang et al., 2012b). The influence of  
145 cations on the behaviour of CNMs is well illustrated by the extent to which physical straining  
146 (filtering out) of  $nC_{60}$  occurs in saturated porous media. Zhang et al. (2012a) found that columns of  
147 pure quartz resulted in very limited nanoparticle deposition even at low flow velocities, whereas a

148 heterogeneous sandy soil with low OM content and small, irregular and rough grains of sand,  
149 significantly inhibited  $nC_{60}$  transport. With the addition of  $CaCl_2$ , greater deposition of  $nC_{60}$  was  
150 observed in both sand and soil; however, significantly more straining occurred in the soil due to  
151 the greater number of complexation sites for  $Ca^{2+}$  clay and OM fractions relative to sand (Zhang et  
152 al., 2012a). For both the sand and soil columns,  $Ca^{2+}$  had a much larger effect on the transport of  
153  $nC_{60}$  than  $Na^+$  at the same ionic strengths (Zhang et al., 2012a). This most likely occurred due to  
154 efficient neutralisation of surface charges on both  $nC_{60}$  and sand and soil particles by  $Ca^{2+}$  relative  
155 to  $Na^+$ , which reduced the electrostatic repulsion (Kuznar and Elimelech, 2004; Zhang et al.,  
156 2012a).

157 When considering the fate and behaviour of CNMs in soils, solid peat may have a different  
158 impact to that of molecular DOM under environmentally relevant ionic conditions. This could be  
159 caused by the alteration of particle phase distributions due to the direct sorption of CNMs, as well  
160 as the possibility of DOM or cations being release from the soil particles themselves (Zhang et al.,  
161 2011a). In the absence of sodium ions, Zhang et al. (2011a) found no adsorption of MWCNTs to  
162 solid peat, indicating a limited affinity of DOM-MWCNT composites towards the solid phase  
163 relative to the aqueous phase, possibly due to electrostatic repulsion and hydrophilicity of DOM  
164 coated nanotubes. With the addition of  $Na^+$  ions, the relative affinity between DOM-MWCNTs and  
165 peat was increased due to reductions in the charge potential and subsequent increase in  
166 interactions occurring through hydrophobic interactions and/or vdW attraction (Zhang et al.,  
167 2011a). Zhang et al. (2011a) concluded that with increasing ionic strength (such as in  
168 environments containing seawater or hard freshwater), an increased precipitation of MWCNTs  
169 from the aqueous phase will occur, impeding their transport within the environment.

170 Consideration of the  $\zeta$ -potential (diffuse surface charge) of CNMs in relation to the soil matrix  
171 is important when considering the dynamics of smaller particles dispersal, transport and  
172 deposition, for which charge forces are likely to be highly influential relative to larger particles or  
173 agglomerates (Darlington et al., 2009). Its measure, in part, provides information on the likely

174 mobility, rates of interaction and aggregation status due to electrostatic forces generated by  
175 charged surfaces (Hu et al., 2005; Jafar and Hamzeh, 2013). Pristine CNTs typically express limited  
176 surface charge (Mohanty et al., 2007); however, Wang et al. (2008a) found that the  $\zeta$ -potential of  
177 CNTs with a HA coating was highly negative, which resulted in electrostatic repulsion between the  
178 particles and hence stability when partitioned into the aqueous phase. They concluded that  
179 mobility and environmental transport within typically negatively charged porous media, such as  
180 certain types of soils was highly likely, with particles remaining stable over a wide range of ionic  
181 strengths (Wang et al., 2008a). A reduction in pH to the point at which the CNTs had no charge  
182 was identified as an effective means of causing CNTs to precipitate, through the destabilization of  
183 the HA coatings (Wang et al., 2008a).

184 The properties of the humic substances determine the extent to which DLVO and non-DLVO  
185 interactions influence particle behaviour. TA (Chibowski et al., 1998) and HA sorbed to CNTs  
186 enhances stabilisation in water through reducing vdW forces between particles and increasing  
187 steric repulsion (Terashima and Nagao, 2007; Ren et al., 2011). However, Qu et al. (2012)  
188 identified that high molecular weight (HMW) HAs were more effective in promoting suspension  
189 stability due to stronger steric repulsion than that of low molecular weight (LMW) HAs. Similarly,  
190 HAs containing large quantities surfactive domains, such as those which are strongly hydrophilic  
191 and lipophilic, promote the dispersal of CNTs in solutions, while those containing carbohydrates  
192 and predominantly hydrophilic domains resulted in limited dispersal (Chappell et al., 2009).

193 The composition of SOM in relation to ionic strength and pH dictates the behaviour of CNMs  
194 within soils. Presently, however, insufficient data regarding the relative impact of different SOM  
195 fractions and combinations on DLVO and non-DLVO forces in soils is lacking, reducing an ability to  
196 estimate how CNMs may behave based on analysis of soil OM content. Furthermore, in addition  
197 to the organic fraction of soils and coating of CNMs, the role of the inorganic fraction in  
198 determining particle behaviour must also be considered.

199 *3.2 The impact of soil inorganic matter*



200 In addition to the organic fraction, CNM stability in saturated soil/water suspensions is  
201 strongly influenced by the impact of the inorganic fraction, and is largely neglected within the  
202 present literature. Han et al. (2008) studied the impact of kaolinite and montmorillonite clay  
203 minerals with particle sizes of around 2  $\mu\text{m}$  on the stability of MWCNTs ( $18 \text{ mg l}^{-1}$ ) suspended in  
204 three different surfactants (either cetyltrimethylammonium bromide (CTAB),  
205 dodecylbenzenesulfonic acid, sodium salt (SDBS), or octyl-phenol-ethoxylate (TX100), each at 40  
206  $\text{mg l}^{-1}$ ). The study showed that MWCNTs stabilised by CTAB, became deposited in the presence of  
207 montmorillonite or kaolinite particles, which suggests MWCNTs may not move through soils or  
208 sediments containing these minerals, or that the addition of montmorillonite or kaolinite could be  
209 used to reduce their mobility and transport (Han et al., 2008). However, no investigation such as  
210 soil column leach testing was performed to specifically measure the movement of MWCNTs, and  
211 further direct measurements are required to verify the results in soils. Suspensions of CNTs in  
212 SDBS were not affected by the presence of either montmorillonite or kaolinite, and TX100  
213 suspensions were not altered by kaolinite, but destabilised partially in montmorillonite (Han et al.,  
214 2008). The authors suggested that CNTs may be able to move through soils and sediments  
215 containing these clay minerals if suspended using SBS or TX100. It was proposed that the  
216 destabilisation of surfactant-dispersed MWCNTs occurs by two mechanisms; (i) removal of  
217 surfactants from solution by clay minerals and (ii) clay minerals bridging between MWCNTs and  
218 surfactants (Han et al., 2008).

219 Furthermore, the charge characteristics of soils can also influence the behaviour and fate of  
220 CNMs. Broadly, all soils can be divided into two groups; permanent-charge (P-C) and variable-  
221 charge (V-C) (Sollins et al., 1988). In P-C soils, the substitution of ions with lower valence for ions  
222 with higher valence results in the alteration of crystal lattice structures within layer-silicate clays  
223 (illite, smectite, chlorite and kaolin), and a permanent charge deficit, which persists irrespective of  
224 variations in the composition of soil solutions and pH (Sollins et al., 1988). In V-C soils, protonation  
225 and de-protonation of surface hydroxyl groups results in the positive charge and hence anion

226 exchange capacity (AEC); whereas deprotonation results in cation exchange capacity (CEC) (Sollins  
227 et al., 1988). The structure of V-C soils is also modified in response to increasing pH, resulting in  
228 increased repulsion and more limited aggregation (Sollins et al., 1988). Both P-C and V-C surfaces  
229 are present in all soil types; however, only one charge system typically dominates, dictated largely  
230 by soil mineralogy (Sollins et al., 1988). While V-C soils occur more frequently in tropical regions  
231 due to the typical mineralogical composition which forms under humid, warm conditions, they do  
232 not occur ubiquitously, and many areas with predominantly P-C characteristics occur (Sanchez,  
233 1976; Sollins et al., 1988). Hence, while V-C soils represent a small fraction of global soil types,  
234 interactions between nanoparticles and soils are likely to be much more dynamic relative to those  
235 with a P-C. Despite this, almost all investigations have predominantly focused on P-C soils,  
236 restricting the applicability of CNM fate and behaviour investigations.

237       The behaviour of CNMs in V-C soils has been assessed by Zhang et al. (2012b), who  
238 investigated the stability of MWCNTs suspended in water with soil minerals kaolinite, smectite  
239 and shale over a range of sodium concentrations. Without additional Na<sup>+</sup>, no significant difference  
240 in the stability of MWCNTs between each of the soil minerals was observed; however, with  
241 increasing ionic strength, the removal of MWCNTs from the aqueous phase followed the order  
242 smectite > kaolinite > shale (weakest to largest MWCNT association). As ionic strength increased,  
243 the MWCNT removal tendency for smectite and kaolinite was inversely correlated to the mineral  
244 surface potential. However, the electrostatic potential of shale is higher than either kaolinite or  
245 smectite, yet shale demonstrated the strongest sorption of MWCNTs (Zhang et al., 2012b). This  
246 was attributed to the large, hydrophobic, organic content of shale, which is able to strongly sorb  
247 MWCNTs. Hence, under these soil conditions, the transport of CNMs in soils is directly correlated  
248 with mineral hydrophobicity, but inversely correlated with surface potential (Zhang et al., 2012b).  
249 It is therefore imperative that studies of nanomaterial fate and behaviour in soils include detailed  
250 information regarding soil mineralogy.

251 *3.3 The impact of CNM preparation methods, functional groups and UV exposure*

252 In addition to the influence of soil type and properties, the properties of CNMs themselves  
253 vary greatly depending on an array of parameters. As commercial applications of CNMs will likely  
254 employ surface functional groups and a variety of different preparation techniques, nanoparticle  
255 properties and behaviour within the environment will become increasingly complex (Turco et al.,  
256 2011). For example, the physicochemical properties of pristine  $nC_{60}$ , such as surface charge and  
257 particle size, heavily depends on the method of preparation, with a corresponding impact upon  
258 the stability of the nanomaterial (Chen and Elimelech, 2008; 2009; Isaacson et al., 2011). As  
259 discussed previously, deposition and aggregation of CNMs in their pristine state is highly  
260 susceptible to variations in soil water ionic strength; however, the exact extent of sensitivity is  
261 known to vary significantly according to the method of preparation. For example, in an aqueous  
262 solution, the deposition of  $nC_{60}$  occurs in NaCl at concentrations of 18 mM when prepared by  
263 sonication (100 W probe, 30 min) (Qu et al., 2012) and 30 and 32 mM NaCl when prepared by  
264 solvent exchange methods (Chen and Elimelech, 2008; Smith et al., 2008). However, most  
265 investigations have been conducted in simple solutions of electrolytes using pristine  $nC_{60}$ , and in  
266 complex environmental systems (Qu et al., 2012). As a result, the effects of cation valence on the  
267 stability of CNMs may substantially differ to those in a laboratory setting.

268 Typically, agglomeration of CNMs in the presence of divalent ( $Ca^{2+}$ ) cations occurs to a greater  
269 extent than with monovalent ( $Na^+$ ) cations. However, when exposed to solar irradiation,  $nC_{60}$  can  
270 undergo surface oxidation and decomposition (Hou and Jafvert, 2008; 2009), with large  
271 implications for environmental behaviour and fate (Qu et al., 2012). Following exposure to UV-A  
272 (the largest component of UV in sunlight), the oxygen containing functional groups formed on  
273  $nC_{60}$  hindered aggregation in NaCl solutions due to their elevated hydrophilicity and negative  
274 surface charge (Hou and Jafvert, 2009). Conversely, neutralisation of the negative surface charge  
275 on oxidised  $nC_{60}$  due to interactions with  $Ca^{2+}$  ions when suspended in  $CaCl_2$  can result in particle  
276 agglomeration (Li and Liang, 2007). This potentially occurs due to the charge screening ability of  
277  $Ca^{2+}$  relative to  $Na^+$ , which reduces the stability of colloids (Li and Liang, 2007). Qu et al. (2012)

278 expanded upon this work through studying the effects of UV-A exposure for either 20 h or 7 d on  
279 the rate of deposition and the attachment efficiency of  $nC_{60}$  on to silica bead surfaces. The  
280 stability of  $nC_{60}$  increased proportionally with increasing UV-A exposure time against aggregation  
281 in solutions containing NaCl, which was attributed to the increase in surface oxidation and  
282 hydrophilicity (Qu et al., 2012). Further, while the attachment efficiency of  $nC_{60}$  exposed to UV-A  
283 for 7 d was at a maximum in NaCl concentrations of 250 mM, attachment decreased following an  
284 increase in NaCl concentration to 300 mM. This indicates that stability of  $nC_{60}$  containing oxygen  
285 surface functional groups was attributed to the hydration force and not DLVO forces, which was  
286 more significant with the 7 d UV exposed  $nC_{60}$  than either the pristine or the 20 h UV due to the  
287 greater hydrophilicity (Qu et al., 2012).

288 In other investigations, surface immobilisation of macromolecules, such as HAs at  
289 environmentally relevant concentrations, has increased the solubility of  $C_{60}$  due to the effect of  
290 steric hindrance caused by the sorbed SOM and a reduction in the hydrophobicity of the  
291 nanoparticle surface, preventing re-aggregation and reducing attachment efficiency (Li et al.,  
292 2009; Qu et al., 2012). However, Qu et al. (2012) found 7 d UV exposed  $nC_{60}$  had negligible surface  
293 sorption of either HWM or LMW HAs due to the negative surface charge and elevated surface  
294 hydrophilicity. Hence, DOM is likely to be less significant in determining the suspension stability of  
295 irradiated  $nC_{60}$  (Qu et al., 2012). A similar relationship may occur due to the formation of oxygen  
296 containing hydroxyl- and carboxyl-groups on MWCNTs due to surface oxidation, which can  
297 promote colloidal stability and hydrophilicity of CNTs in addition to inducing alterations to surface  
298 charge (Shieh et al., 2007; Smith et al., 2009). This is illustrated by Hu et al. (2005), in which  
299 carboxylic acid groups as a result of nitric acid treatment of SWCNTs had high  $\zeta$ -potentials (-28  
300 mV) over a pH range of 2-10, indicating their moderate stability in water in contrast to pristine  
301 CNTs (Hu et al., 2005). Reduced deposition of pristine  $nC_{60}$  occurred on silica glass beads coated in  
302 HMW HA than LMW HA due to steric hindrance (Qu et al., 2012). The effect was more  
303 pronounced at lower ionic strengths due to electrostatic repulsion between charge groups

304 resulting in a more stretched-out conformation of HA molecules (Qu et al., 2012). However, both  
305 HMW and LMW HA coated beads facilitated the deposition of 7 d UV exposed  $nC_{60}$ , with reduced  
306 sensitivity to changes in ionic strength as a result of reduced steric hindrance (due to the compact  
307 conformation of HAs at high ionic strengths ( $\sim 60$  mM)), lower surface potential and increased  
308 hydrogen bonding between the oxygen containing groups of the functionalised  $nC_{60}$  and nitrogen-  
309 and oxygen-groups on the HA (Qu et al., 2012).

310 Comparatively determining the relative importance of CNM functionalization and ionic  
311 strength on CNTs and  $nC_{60}$  behaviour in soils is difficult due to the myriad of different  
312 experimental configurations. To overcome this, Jaisi and Elimelech (2009) used carboxyl-  
313 functionalised SWCNTs and  $nC_{60}$  (radius of 51 nm) in natural soil columns containing 29% clay and  
314 pore sizes of 22  $\mu\text{m}$ , to determine the impact of ionic strength on particle transport and  
315 deposition. As ionic strength increased (0.03 – 100 mM), the rate of SWCNT deposition within the  
316 soil column also increased, with the observed effect more apparent with divalent cations ( $\text{Ca}^{2+}$ )  
317 than monovalent cations ( $\text{K}^+$ ). Interestingly, while  $nC_{60}$  was highly sensitive to variations in ionic  
318 strength, far lower deposition rates were observed. It was proposed that the structure and shape  
319 of SWCNTs, in particular their large aspect ratio and bulky agglomerated states, in addition to soil  
320 particle heterogeneity increased the straining effect and retention by the soil matrix (Jaisi and  
321 Elimelech, 2009). Nanomaterial structural conformation is therefore a further consideration in the  
322 relative extent to which CNMs will be dispersed and transported within the soil, with  $nC_{60}$  more  
323 likely to experience leaching than SWCNTs under a variety of solution chemistries (Jaisi and  
324 Elimelech, 2009) within negatively charged soil media.

325 Functionalization status is therefore a fundamental consideration to the behaviour of CNMs,  
326 resulting in distinct characteristics, which significantly modify behaviour in relation to their un-  
327 functionalised counterparts. However, key questions as to the behaviour of CNMs within the  
328 environment remain unaddressed; for example, how does the repeated exposure of CNMs to  
329 weathering cycles within the soil influence their fate and behaviour?

330

331 **4. CNM-contaminant sorption, desorption and mobility in soils**

332 The ability of natural colloids to assist in the transport of organic contaminants has been well  
333 documented and reviewed (de Jonge et al., 2004; Sen and Khilar, 2006; Li et al., 2013). Typically,  
334 hydrophobic compounds such as PCBs and PAHs have limited environmental mobility due to  
335 strong sorption to SOM. Kan and Tomson (1990), however, demonstrated that high  
336 concentrations of colloidal materials such as DOM may enhance the transport of hydrophobic  
337 compounds such as phenanthrene and naphthalene by a factor of a thousand or greater, with  
338 possible implications for the spread of contamination and groundwater quality (de Jonge et al.,  
339 2004). Although CNMs may be tailored to suit specific requirements, their behaviour is not  
340 necessarily different to colloids naturally occurring in the environment (Colvin, 2003; Lead and  
341 Wilkinson, 2006). To determine the relevance of natural nanoparticle facilitated transport of  
342 contaminants in porous media such as soils, Kretzschmar et al. (1999) identified four key factors  
343 that will be used as a framework for this section:

- 344 1) Sufficiently high concentration of nanoparticles
- 345 2) Mobility of the nanoparticles carrying sorbed HOCs
- 346 3) Sorbate toxicity even when present in trace quantities
- 347 4) The ratio of sorption to desorption relative to the timescale of particle mobility

348 The sorption affinity of CNMs for common environmental contaminants such as PAHs, known  
349 to pose significant risks to both the environment and human health due to their toxic properties  
350 (Menzie et al., 1992; Shaw and Connell, 1994; Cebulska-Wasilewska et al., 2007), has been  
351 reported as over three orders of magnitude greater than that of natural soil/sediments (Yang et  
352 al., 2006b). The potential for these emerging materials to become widespread in the soil  
353 environment, particularly those with a strongly hydrophobic nature and large reactive surface

354 area, such CNMs, raises questions and concerns about the environmental consequences of their  
355 release (Pan and Xing, 2010).

#### 356 *4.1 CNM contaminant sorption and desorption in soils*

357 Understanding the adsorption and desorption of HOCs to CNMs in soils is critical to the  
358 environmental risk assessment processes, as well as determining their potential applications as  
359 environmental adsorbents (Yang et al., 2006a). As the fundamentals of CNM-HOC sorption have  
360 been extensively reviewed, the reader is referred to a review by Ren et al. (2011) for a  
361 comprehensive overview. This section addresses the manner in which soils may alter the HOC  
362 sorption/desorption properties of CNMs, focusing specifically on two conflicting effects; (i) CNM  
363 dispersal by DOM (increasing the surface area and hence the number of adsorption sites (Hyung  
364 et al., 2006; Lin and Xing, 2008)); versus (ii) the formation of CNM-DOM coatings (blocking and/or  
365 competing for adsorption sites reducing the number available for organic contaminants (Chen et  
366 al., 2008; Wang and Keller, 2009; Cui et al., 2011; Wang et al., 2011; Zhang et al., 2011c)). The  
367 relative importance of these two phenomena are poorly understood in relation to their sorption  
368 and desorption of organic contaminants (Zhang et al., 2011c; Pan and Xing, 2012), and are highly  
369 dependent on the nanoparticle properties, and the nature of SOM and the sorbate (Wang et al.,  
370 2009; Zhang et al., 2011c; Lerman et al., 2013).

371 In assessing the impact of OM on CNM sorption in the environment, further complications  
372 arise as contaminants are able to sorb to both the CNM and CNM-OM coating (Wang et al.,  
373 2008b). Hyung and Kim (2008) identified SOM adsorption to nanotubes was highly variable  
374 depending on the type of SOM, occurring proportional to its aromatic carbon content. This has  
375 implications for determining the ability of CNMs to sorb organic compounds, yet most  
376 investigations fail to consider the role of different OM fractions in CNT-pollutant interactions  
377 (Lerman et al., 2013).

378 Wang et al. (2008b) assessed the extent to which HAs and peptone altered the sorption of  
379 phenanthrene, naphthalene or 1-naphthol on-to MWCNTs (outer diameter of 40 nm), by fitting  
380 sorption data with Freundlich and Polanyi models. Their results showed that each type of DOM  
381 resulted in nonlinear sorption isotherms to the MWCNTs, following the order peptone > HAs.  
382 Although the inherent sorptive ability of HA for each of the contaminants was more limited than  
383 that of pristine MWCNTs, HA coatings did not result in large changes to the sorption of any of the  
384 contaminants, which is inconsistent with models indicating that “fouling” of sorption sites by  
385 DOM will reduce contaminant sorption capacity (Carter and Weber, 1994; Wang et al., 2008b).  
386 The authors proposed that either uneven coating of the MWCNT by HA occurred, or that the  
387 anticipated sorption reduction as a result of polar moieties from the HA coating, was offset due to  
388 the increase in O-containing moieties resulting in particle repulsion and dispersal, exposing new  
389 sites available for HOC sorption. Contrastingly, peptone, due to the large quantity sorbed relative  
390 to each of the other DOM fractions, resulted in the largest reduction in available sorption sites  
391 (Wang et al., 2008b). Similar interactions as to the relative ability of different OM coatings to alter  
392 CNM sorption have been identified by Cui et al. (2011) and Gai et al. (2011). Although direct  
393 comparison of the studies is not possible due to the different particles used, Cui et al. (2011)  
394 found HAs, TAs and peptone pre-interacted with SWCNTs resulting in the formation of polar  
395 functional groups on the nanotube surface, reducing the area available for phenanthrene sorption  
396 in the order of peptone > TAs > HAs. Similarly, Gai et al. (2011) identified a reduction in C<sub>60</sub>  
397 agglomerate sizes due to the dispersal effects of HA, increasing atrazine sorption due to dispersal  
398 and re-arrangement, rather than interactions between the atrazine and HA (Gai et al., 2011).  
399 Hence, it may be argued that the impact of DOM on CNM-HOC sorption is dependent on the type  
400 of OM present and possibly also CNM type.

401 Within a soil environment, Li (2012), identified the sorption behaviour of naphthalene,  
402 phenanthrene and fluorine in a sandy loam soil, silt loam soil and Ottawa sand was unaffected  
403 following amendment of MWCNTs at concentrations of 2 mg g<sup>-1</sup>. For each contaminant



404 investigated, sorption in both the MWCNT amended and unamended samples followed the same  
405 order; silt loam > sandy loam > sand, indicating the sorptive ability was driven by the organic  
406 carbon content (Li, 2012). Additionally, no difference between sorption isotherms of MWCNT  
407 amended and unamended samples was apparent, indicating that MWCNTs held no influence over  
408 the samples inherent sorption capacity (Li, 2012). Similarly, the order in which PAHs sorbed was  
409 unaffected by the MWCNTs, occurring as anticipated according to the PAHs  $K_{ow}$  values (Li, 2012).  
410 After 24 h hydroxypropyl- $\beta$ -cyclodextrin (HPCD) desorption, no statistically significant differences  
411 in the percentage desorbed were detected between nanotube amended and unamended  
412 samples. Hence, the sorptive properties of MWCNTs in the environment may be similar to hard  
413 carbon, and did not influence the sorption/desorption behaviour of PAHs (Li, 2012). When this is  
414 related to Factor 4 proposed by Kretzschmar et al. (1999), in which the sorption to desorption  
415 ratio over timescale of particle transport is considered, MWCNTs at  $2 \text{ mg kg}^{-1}$  concentration may  
416 not be considered significant in determining the behaviour of some PAHs in soils over the  
417 duration of their experiment. It may be, however, that Factor 1 was not met, and the lack of  
418 MWCNT-influence on PAH behaviour was merely a result of an insufficient quantity added to the  
419 soils, although a concentration of  $2 \text{ mg kg}^{-1}$  in environmentally relevant terms is likely to be  
420 unrealistically high. Hence, while this study indicates the sorption of multiple contaminants in the  
421 different soil types considered will not present an environmental concern in terms of pollutant  
422 mobilisation at  $2 \text{ mg kg}^{-1}$ , it was not possible to consider the desorption of contaminants if  
423 transport were to occur.

424 An excellent study by Towell et al. (2011), assessed the extent to which HPCD extraction of  
425 HOCs with different physicochemical properties desorbed from soils amended with CNMs at  
426 concentrations between 0.05% and 0.5% (substantially larger than that employed by Li (2012)). At  
427 concentrations  $\geq 0.05\%$ , Towell et al. (2011) identified significantly less  $^{14}\text{C-B}[\alpha]\text{P}$  extracted from  
428 CNM amended soils than  $^{14}\text{C}$ -phenanthrene due to the high hydrophobicity and  $\log K_{ow}$  value  
429 reducing the ability of  $^{14}\text{C-B}[\alpha]\text{P}$  to partition into the aqueous phase. This was exacerbated by the

430 relatively HMW of  $^{14}\text{C}$ -B[a]P, which has been proven as a critical factor determining the bonding  
431 energy between SWCNTs and PAHs (Debnath et al., 2008; Towell et al., 2011). In relation to Factor  
432 4, the nature of the sorbate may therefore influence the extent of desorption, and therefore the  
433 duration for which contaminants will remain sorbed. It may be proposed that CNM sorbed HMW  
434 HOCs represent a greater risk of increased distance of transportation within the environment than  
435 LMW HOCs.

436 While sorption of HOCs to CNMs in soils can occur, the extent of sorption and desorption is  
437 dependent on the type of OM and concentration of CNMs. With a view to the manner in which  
438 the properties outlined above potentially facilitate transportation of contaminants sorbed to  
439 CNMs in soils, studies in which mobility has been directly investigated will also be discussed.

#### 440 *4.2 CNM-HOC mobility*

441 Once sorbed to freely suspended CNMs within the soil matrix, the mobility of HOCs is  
442 potentially increased; however, very few studies have focused on determining the impact of  
443 CNMs on contaminant movement in soils. An overview of the basic principal of CNM facilitated  
444 HOC transport is presented in Figure 1. Using column leach tests, Li (2012) examined the  
445 behaviour of phenanthrene, fluorine, naphthalene and pyrene in a saturated sandy loam soil  
446 amended with MWCNTs, functionalised MWCNTs (f-MWCNTs) and functionalised SWCNTs (f-  
447 SWCNTs) at a concentration of  $5 \text{ mg kg}^{-1}$ . Significant retention of PAHs within the soil column was  
448 observed, due to the strong sorption of contaminants by CNTs and their limited mobility within  
449 the soil column (Li, 2012). In control soils and those amended with MWCNTs and f-MWCNTs,  
450 retention of PAHs occurred in the order naphthalene < fluorine < phenanthrene < pyrene, with  
451 hydrophobic interactions between the CNTs and PAHs cited as the predominant cause of the  
452 observed pattern (Li, 2012). Contrastingly, retention of contaminants within soils amended with f-  
453 SWCNTs occurred in the order of naphthalene > fluorine > phenanthrene > pyrene, the sorption of  
454 which could not be accounted for by hydrophobic forces alone (Li, 2012). The trend was  
455 negatively correlated to molecular size, indicating that larger sorbate molecules may have less

456 space for sorption due to the additional hydrophilic functional group (Yang et al., 2006b; Li, 2012).  
457 It was concluded that leaching behaviours were determined by physical characteristics of both  
458 CNTs and contaminants (Yang et al., 2006b; Li, 2012).

459 To determine the extent to which CNMs facilitated the movement of contaminants relative to  
460 various types of DOM, Zhang et al. (2011b) used saturated, sandy soil columns contaminated with  
461 either PCBs or phenanthrene to comparatively assess the mobilising ability of  $nC_{60}$  at 1.55 – 12.8  
462  $mg\ l^{-1}$  relative to DOM at 10-11  $mg\ l^{-1}$ . In this experiment, PCB (12.4 – 13.9  $\mu g\ l^{-1}$ ) or phenanthrene  
463 (14.8  $\mu g\ l^{-1}$ ) was added to a sonicated suspension of  $nC_{60}$  (1.55 - 12.8  $mg\ l^{-1}$  in electrolyte solution  
464 of 0.5 mM NaCl), and tumbled end-over-end (3 rpm) for 7 d to reach adsorption equilibrium. The  
465 suspension was then added to the columns. The results showed that even the lowest  
466 concentration of  $nC_{60}$  significantly enhanced the dispersal of both PCB, and phenanthrene;  
467 whereas, columns containing only various types of DOM had no effect on contaminant transport  
468 (Zhang et al., 2011b). The enhanced contaminant mobilisation ability of  $nC_{60}$  relative to naturally  
469 occurring DOM was attributed to its unique porous structure and surface enthalpies of  
470 interaction, which generate a large sorption affinity together with an irreversibly or slowly  
471 desorbable fraction of adsorbed phenanthrene/PCBs (Hofmann and von der Kammer, 2009;  
472 Zhang et al., 2011b; Wang et al., 2012a). CNMs may therefore be much more efficient at  
473 enhancing the mobility of contaminants than natural colloidal materials.

474 Different processes of  $nC_{60}$  formation have also been identified as contributing to large  
475 differences in their ability to alter the fate and transport of contaminants (Wang et al., 2012b).  
476 Wang et al. (2012b) assessed  $nC_{60}$  samples prepared using either the standard solvent exchange  
477 method, eight different types of SOM or surfactant modifications, or by the phase-transferring of  
478  $nC_{60}$  from a solution of toluene to either SOM or a surfactant (Wang et al., 2012b). Their results  
479 indicated that while the mobility of  $nC_{60}$  was similar between each of the preparation methods,  
480 the contaminant mobilising capability significantly differed. Relative to the unmodified  $nC_{60}$ ,  
481 transport of PCBs through a saturated column of sandy soil increased by 42.2 – 227% with

482 surfactant modified  $nC_{60}$ , and by 233-370% with SOM-modified samples (Wang et al., 2012b). The  
483 results were attributed to both increased adsorption affinities together with enhanced resistance  
484 to desorption due to alterations to  $nC_{60}$  aggregation properties as a result of the SOM surfactant  
485 (Wang et al., 2012b). During the process of aggregate formation, it is possible that a fraction of  
486 SOM or another surfactant was intercalated within the  $C_{60}$  aggregates, significantly influencing the  
487 porosity and geometry of the resulting  $nC_{60}$  aggregates, contributing to the enhanced desorption  
488 resistance of PCBs (Wang et al., 2012b). With differing types of SOM and surfactants, variations in  
489 the quantity and geometry of pores will occur, with the possibility that  $nC_{60}$  could be tailored to  
490 specific physicochemical properties for use in *in situ* site remediation (Wang et al., 2012b). Hence,  
491 the adsorption, desorption and transport of contaminants by  $nC_{60}$  will vary greatly depending on  
492 the condition of its formation (Wang et al., 2012a).

493 Using a different approach, Hofmann and von der Kammer (2009) computer modelled the  
494 extent to which CNMs could result in the movement of HOCs in soils under various scenario-based  
495 conditions, to determine when relevant CNM transport of sorbed HOCs might occur. Worst-case  
496 scenarios were adopted, assuming fully mobile CNMs within the porous medium, over a range of  
497 realistic yet high CNM concentrations ( $100 \text{ mg L}^{-1} - 1 \text{ g}^{-1}$ ) occurring in aggregate sizes of 10 – 100  
498 mm. It was also assumed that CNMs were pre-equilibrated with the HOC at source and that  
499 diffusion was the rate-limiting step for desorption (Hofmann and von der Kammer, 2009). From  
500 this, it was possible to estimate the fraction of contaminants bound to CNMs at different  
501 distances from the source over different time periods (days to years) using the Streamtube Model  
502 for Advective and Reactive Transport (SMART) (Finkel et al., 1998), combined with the application  
503 of retarded pore diffusion approximations (Bold et al., 2003) and combinations of two first-order  
504 rate expressions (Cornelissen et al., 1997). The results showed that for aggregates of 100 mm, 2,  
505 7, 40, 75, 82% of bound contaminants were transported > 1 m at nanoparticle concentrations of  
506 0.1, 1, 10, 100, 1000  $\text{mg l}^{-1}$ , respectively. Conversely, modelled transportation of contaminants  
507 sorbed to aggregates of 10 mm in size were reduced to 0.1, 0.5, 3.6, 8% for the same respective

508 concentrations. Breakthrough of the 1 m modelled column did not occur in any of the considered  
509 scenarios and all contaminants remained bound to the nanoparticle.

510 Parameterisation of the ratio of desorption to sorption and particle transportation is achieved  
511 by the Damköhler number (Da) (Equation 1) (Jennings and Kirkner, 1984), and was employed to  
512 simulate the HOC desorption from CNMs.

513 **Equation 1**

514  $Da_{NP} = \lambda s$

515 Where  $Da_{NP}$  = Damköhler number for the NP,  $\lambda$  = rate constants (first order) for the reaction in  
516  $s^{-1}$ ,  $s$  = average residence time within the system, which may also be expressed as average flow  
517 velocity (Hofmann and von der Kammer, 2009). A ratio of 0 identifies equilibrium between  
518 particle-contaminant interactions, whereas 1 indicates a decoupled transport (i.e. the HOC in  
519 solution will be transported independent of contaminants sorbed to the CNM) and  $< 0.01$   
520 indicates fully decoupled transport. In these instances, HOCs sorbed to CNMs will not desorb over  
521 the transportation time frame, rather relocate within the media (Hofmann and von der Kammer,  
522 2009). At  $Da_{NP}$  numbers  $> 100$ , an equilibrium exists between the immobile porous media and  
523 mobile CNM (Kretzschmar et al., 1999; Bold et al., 2003), resulting in limited nanoparticle  
524 relocation of the contaminant (Hofmann and von der Kammer, 2009).

525 Hofmann and von der Kammer (2009) calculated Damköhler numbers for CNM aggregates of  
526 different sizes and partitioning coefficients according to the rate constant data shown in Figure 2,  
527 and based on different flow velocities of 1 m in 50 d (fast flow) – 1 m in 10 y (slow movement). It  
528 was inferred that the CNM-contaminant transport mechanisms are strongly dependent on the  
529 size of CNM agglomerates together with the distribution coefficients ( $\log K_d$ ) (Hofmann and von  
530 der Kammer, 2009). For example, Figure 2 shows contaminants sorbed to 1 mm aggregates at a  
531 flow velocity of 1 m 50 d<sup>-1</sup> will not experience contaminant desorption until the  $\log K_d$  of HOC-  
532 CNMs is 8 m<sup>3</sup> kg<sup>-1</sup>, reaching equilibrium at  $\log K_d$  1 m<sup>3</sup> kg<sup>-1</sup> (Hofmann and von der Kammer, 2009).

533 However, at a flow velocity of  $1 \text{ m y}^{-1}$ , decoupled transport will predominate for 1 mm aggregates  
534 at a  $\log K_d$  of  $9 \text{ m}^3 \text{ kg}^{-1}$  reaching equilibrium at  $\log K_d$  of  $2 \text{ m}^3 \text{ kg}^{-1}$  (Hofmann and von der Kammer,  
535 2009). It was concluded that under equilibrium sorption/desorption conditions, CNM mobility  
536 resulted in negligible transport of sorbed contaminants (Hofmann and von der Kammer, 2009).  
537 However, the mobility and concentration of CNMs becomes increasingly important in instances  
538 with slow to very slow desorption (Hofmann and von der Kammer, 2009). While there are many  
539 assumptions and simplifications associated with every modelling technique, the model identifies  
540 scenarios in which transport and desorption of sorbed contaminant could potentially occur,  
541 possibly providing useful guidelines for risk-assessment if applied on a case by case basis.  
542 However, further work aimed specifically at validating the model against traditional column leach  
543 tests in both V-C and P-C soils and additional desorption kinetics are urgent prerequisites.

544 From the above discussion, it can be concluded that each of the four factors identified by  
545 Kretzschmar et al. (1999) for significant transport of contaminants by CNMs have been met.  
546 However, more work examining the subsurface transport of CNMs through well-defined soils of  
547 various types (such as clays, peats and silts) and CNMs with a variety of functional groups, sizes  
548 and sorbed compounds in both saturated and unsaturated conditions are required (Jaisi and  
549 Elimelech, 2009; Petersen et al., 2011). Of studies that are available, variation in experimental  
550 conditions between the investigations renders comparisons of the efficiency of contaminant  
551 mobility between CNM types tentative until standardised comparative testing is conducted.  
552 Additionally, the molecular weights and sizes of CNMs may not be constant during their transport  
553 within the soil environment, due to their physical, chemical or biological interaction with soil  
554 components, which will likely influence their aggregation status, shape, surface charge (Pan and  
555 Xing, 2012), and possibly also their ability to sorb and mobilise contaminants over long timescales.  
556 Furthermore, definitive data of the desorption kinetics of HOCs from CNMs in soils are essential to  
557 understanding their ability to transport contaminants (Ibaraki and Sudicky, 1995; Choi and Yavuz  
558 Corapcioglu, 1997; Corapcioglu et al., 1999; Bold et al., 2003; Hofmann and von der Kammer,

559 2009), with slow desorption identified as a critical requirement (Roy and Dzombak, 1998). The  
560 lack of experimentally derived desorption kinetic data from a range of soil types and conditions  
561 makes determining the extent to which HOC sorption is strong enough, and desorption slow  
562 enough, to allow CNMs to transport sorbed HOCs, and the associated implications of transport,  
563 difficult to predict (Qu et al., 2012).

564

## 565 **5. CNM – microorganism interactions**

566 As soils represent one of the ultimate sinks for nanomaterials (Nowack and Bucheli, 2007),  
567 terrestrial microorganisms, which are a large component of soils, may be significantly affected  
568 (Navarro et al., 2008). The reader is directed to an excellent review by Holden et al. (2014), which  
569 evaluates the possible exposure concentrations of anthropogenic nanomaterials in a range of  
570 environmental compartments, and assesses their relevance. However, understanding the impact  
571 of CNMs on the soil microbial community is a subject still in its infancy (Dinesh et al., 2012). The  
572 extent to which CNMs interact with microflora will (in part) determine the extent of possible  
573 disruptions to bio-geochemical processes within soils that they may cause (Neal, 2008). This  
574 section discusses recent literature related to the modification of CNM fate and behaviour by  
575 microbiota, the toxicity of CNMs in soils and the possible implications for the biodegradation of  
576 contaminants.

### 577 *5.1 Biological modification of CNMs in soils*

578 The influence of microbial populations on the physical and chemical state of nanoparticles  
579 must be considered when discussing the ultimate fate of nanomaterials (Arugueté and Hochella,  
580 2010). Degradation of C<sub>60</sub> in aqueous solutions through photochemical processes have been  
581 identified by numerous investigations (Section 3.3) (Hou and Jafvert, 2008; Lee et al., 2009; Li et  
582 al., 2009), which may be an important step in both its breakdown and the activation of precursors  
583 for subsequent biological interactions (Turco et al., 2011). While C<sub>60</sub> photochemical reactions at

584 the soil surface have not been studied, its oxidation and transformation to the more reactive  
585 fullerol (i.e. C<sub>60</sub>-OH) has been observed in water and in the presence of oxygen (Turco et al.,  
586 2011). Following the abiotic photochemical modification of C<sub>60</sub> through sunlight into fullerols,  
587 white-rot fungi was able to attack and subsequently incorporate a small amount of fullerol carbon  
588 into fungal biomass (lipids) after 32 weeks of decay (Schreiner et al., 2009). By contrast,  
589 unmodified C<sub>60</sub> was recalcitrant to such attack (Schreiner et al., 2009); hence, following minor  
590 surface alterations, biological interactions with C<sub>60</sub> were substantially altered, changing the fate of  
591 the particle. Similarly, the potential for horseradish peroxidase to biodegrade CNTs is strongly  
592 related to the presence of carboxyl groups on the nanotubes surface, which permitted enzyme  
593 mediated oxidation relative to pristine CNTs (Allen et al., 2008; Allen et al., 2009). Furthermore,  
594 Fenton's reagents oxidised carboxyl-functionalised SWCNTs (SWCNT-COOH) through the  
595 formation of hydroxyl radicals (Allen et al., 2008; Allen et al., 2009). It has therefore been  
596 suggested that both white and brown rot mediated fungal activity could modify surface  
597 functionalised CNTs in a similar manner to fullerols (Turco et al., 2011).

598       Ultimately, Turco et al. (2011) suggested that the fate of C<sub>60</sub> in soil is potentially controlled by  
599 the rate of abiotic alterations to the formation of more reactive precursors, as opposed to a  
600 simple dose response, and the toxicity of UV-modified CNMs in soils has not yet been  
601 investigated. If degradation of CNMs by fungi were to occur on a large scale in the natural  
602 environment, their potential environmental risk would be significantly reduced; however, it is  
603 unlikely to occur in sufficiently large quantities to efficiently reduce any possible burden of CNM  
604 presence in soils.

## 605 *5.2 CNM toxicity to soil microorganisms*

606       The toxicity of CNMs is dependent upon the bioaccessibility of nanoparticles to bacteria, and  
607 retention of some the nanoparticles reactivity (Neal, 2008). Currently, little literature is available  
608 related to the toxicity of CNMs within soils (Dinesh et al., 2012). Hence, the discussion presented  
609 here provides a theoretical estimation of the specific microbial communities that may be more



610 vulnerable to soil-borne CNMs, followed by an overview of recent CNM-amended soil toxicity  
611 findings published within the literature.

612 Soil conditions will ultimately dictate the extent to which CNMs are able to interact with  
613 terrestrial microflora. Based on the discussion earlier relating to the fate and behaviour of CNMs  
614 in soils, in addition to information regarding cell properties (Mehmannavaz et al., 2001), it may be  
615 possible to tentatively speculate as to the bioavailability or bioaccessibility of CNMs to different  
616 microbial populations. When assessing nanotoxicity, consideration must be given to both the  
617 likelihood of a nanoparticle coming into contact with microbial cells together with the initial  
618 concentration added to soils, to provide an accurate means of estimating the particle availability  
619 (Dinesh et al., 2012). A strong interplay exists between the dispersal status of nanoparticles and  
620 their bioaccessibility to specific soil microbial populations (Turco et al., 2011). As bacteria  
621 frequently adhere to surfaces in the soil environment, attached cells within biofilms constitute a  
622 large proportion of the bacterial community in the subsurface environment (Neal, 2008). Neal  
623 (2008) therefore proposed that the study of nanotoxicity towards biofilm communities is a more  
624 appropriate measure of toxicity in environmental systems than planktonic cells. However, it is  
625 conceivable that given appropriate DLVO and non-DLVO forces between CNMs, microorganisms  
626 and the soil matrix, CNMs could also become available to planktonic cells. One example of which  
627 may be that CNM-SOM coatings could result in easier access to the cell surface relative to  
628 uncoated particles due to the similarities in solubility between the cell membrane and surfactant;  
629 however, the coating itself may attenuate the toxicity due to a lack of physical contact between  
630 the CNM and a microbial cell (Lubick, 2008). Further work into the conditions under which CNMs  
631 will be available to different microbial communities in soils is needed.

632 The extent to which soils with different properties determine the toxicity of some CNMs was  
633 directly investigated by Chung et al. (2011). The impact of MWCNTs at 50, 500 and 5000  $\mu\text{g}^{-1}$  soil  
634 on the activity of soil microorganisms in a sandy loam (pH 6.98, OC content 17.69  $\text{g kg}^{-1}$ , CEC 13.51  
635  $\pm 0.78$ ) and loamy sand (pH 5.21, OC content 8.33  $\text{g kg}^{-1}$ , CEC 9.05  $\pm 0.10$ ) was considered. Based

636 on an analysis of the activity of enzymes involved with cycling carbon (1,4- $\beta$ -glucosidase,  
637 cellobiohydrolase, xylosidase), nitrogen (1,4- $\beta$ -acetylglucosaminidase) and phosphatase together  
638 with lower microbial biomass-nitrogen and carbon in soil, their results indicated that MWCNTs  
639 exhibited antimicrobial properties within both soil types (Chung et al., 2011). As these findings are  
640 consistent with culture studies outside of the soil environment, in which reduced microbial  
641 activity was a result of membrane damage, physical piercing and oxidative stress (Kang et al.,  
642 2007; Simon-Deckers et al., 2009), the authors assumed that these antimicrobial mechanisms of  
643 action may be responsible, with their impact not attenuated by the different soil properties  
644 investigated.

645 Other investigations of nanotoxicity within soil using  $nC_{60}$  have found more limited toxicity  
646 effects. For example, Johansen et al. (2008) found microbial respiration and biomass to be  
647 unaffected by pristine  $C_{60}$  agglomerates (50 nm – 50  $\mu$ m-size) applied at concentrations of 0, 5, 25  
648 and 50 mg kg<sup>-1</sup> to dry, clay loam textured soil containing 2.5% OM and with a pH of 6.7. However,  
649 polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) measurements of  
650 the diversity and number of bacteria over a 14 d period showed that a three to four fold reduction  
651 in rapidly growing bacteria occurred immediately following the addition of  $C_{60}$  (Johansen et al.,  
652 2008). The authors proposed the results may have been observed as a direct consequence of  
653 reactive oxygen species (ROS) formed by the  $C_{60}$ , which disrupted DNA and lipids within  
654 membranes (Johansen et al., 2008). However, confirmation of ROS damage could not be acquired  
655 due to the complexity of the soil environment (Dinesh et al., 2012), and a recent publication by  
656 Chae et al. (2012) casts some doubt on the extent to which ROS are generated in the presence of  
657 SOM. It may therefore be considered more likely that the observed alterations to the diversity  
658 and number of bacteria may be an indirect result of a reduction in nutrient bioavailability due to  
659 adsorption by  $C_{60}$  (Johansen et al., 2008).

660 In a similar investigation, Tong et al. (2007) assessed the role aggregation status plays in  
661 determining nanotoxicity within soils. The impact of either  $nC_{60}$  at 1  $\mu$ g  $C_{60}$  g<sup>-1</sup> soil, or 1000  $\mu$ g  $C_{60}$  g<sup>-1</sup>

662 <sup>1</sup> soil in granular form on the function and structure of soil microbial community was assessed  
663 (Tong et al., 2007). The silty clay loam soil (pH of 6.9, OM content 4%) was incubated with each of  
664 the nanoparticle treatments for 180 d (Tong et al., 2007). Both C<sub>60</sub> and nC<sub>60</sub> resulted in limited  
665 alteration to either the function or structure of microbial processes or communities (Tong et al.,  
666 2007). These findings are similar to those of Johansen et al. (2008), and consistent with other  
667 investigations in which the bioavailability and antibacterial activity of nC<sub>60</sub> reportedly diminished  
668 following sorption to soil, with the overall sorption capacity dictated by the soil OM content (Li et  
669 al., 2008).

670 Despite differences in experimental setups between the studies by Johansen et al. (2008) and  
671 Tong et al. (2007), from the data presented, it is not possible to rule out the bioaccessibility and  
672 toxicity of C<sub>60</sub> to a proportion of microbiota within soils. Although alterations to microbial  
673 respiration as a result of fullerene addition to soil were not observed in either study, functional  
674 substitution of specific impaired microorganisms may have occurred, masking any apparent  
675 variation (Ekelund et al., 2003; Johansen et al., 2008). The studies presented here provide credible  
676 insight into the possible toxicity of CNMs within the environment; however, insufficient data  
677 comparatively analysing the impact of all CNMs on microbial populations within a range of well-  
678 defined soil types is a major obstacle in determining their potential environmental impact.  
679 Experimental work aimed at addressing the real world implications for particle toxicity to different  
680 microbial communities, systematically testing the factors determining the behaviour and fate of  
681 CNMs in soils highlighted previously, is required before firm conclusions can be drawn regarding  
682 the impact of CNMs on soil microbial activity and structure. Specifically, the implications of abiotic  
683 alterations and methods of CNM preparation on the bioaccessibility and toxicity to soil microbiota  
684 have received little investigation.

### 685 *5.3 The bioavailability and bioaccessibility of CNM associated contaminants*

686 Sorption of contaminants is a fundamental mechanism in the regulation of organic  
687 compound bioavailability (Lou et al., 2011). Given their strong sorptive capability, the addition of

688 CNMs to soil may result in the sequestration of organic contaminants, reducing their extractability  
689 and bioaccessibility, operating in a similar manner to hard or black carbon (Chen et al., 2007).  
690 However, the extent to which the processes identified in Section 4.1 impact upon the  
691 bioaccessibility of contaminants and biodegradation have not received much research within soils.

692 The conditions under which CNMs enter the soil are also critical to determining their impact  
693 upon contaminant bioaccessibility. Zhou et al. (2013) incubated  $^{14}\text{C}$ -2,4-dichlorophenol ( $^{14}\text{C}$ -2, 4-  
694 DCP) in a soil (sandy loam, pH 6.31, 2.5% OC, 46.7% clay, 37.9% silt, 15.4% sand) containing either  
695 0, 2, 20 or 2000  $\text{mg kg}^{-1}$  SWCNTs or MWCNTs to determine the impact of carbon nanomaterials on  
696 the mineralisation, degradation and distribution of  $^{14}\text{C}$ -2,4-DCP in the soil. The impact of the order  
697 in which the nanomaterials were added to the soil was also assessed, with nanomaterials added  
698 either after spiking with  $^{14}\text{C}$ -2,4-DCP, simulating disturbance of CNTs on pre-existing  
699 contamination in soils, or CNMs as a mixture with  $^{14}\text{C}$ -2, 4-DCP, simulating HOC degradation when  
700 carried or accumulated (concentrated) by CNMs within the environment from other sources. The  
701 CNMs were homogenised at using ultrasonication at 90 w, 20 Hz for 5 min in deionised water,  
702 followed by shaking at 100 rpm for 1 day prior to use. The results showed that CNTs added at  
703 concentrations  $\leq 20 \text{ mg kg}^{-1}$  to soil after spiking with  $^{14}\text{C}$ -2, 4-DCP resulted in no significant effects  
704 on the time course of mineralisation, indicating that the activity of microorganisms was not  
705 significantly influenced, nor did the desorption from CNTs reduce  $^{14}\text{C}$ -2, 4-DCP bioavailability in  
706 soil (Zhou et al., 2013). Following the addition of CNTs at 2000  $\text{mg kg}^{-1}$  added after  $^{14}\text{C}$ -2, 4-DCP  
707 spiking, mineralisation of  $^{14}\text{C}$ -2, 4-DCP was significantly ( $P < 0.05$ ) inhibited, which was attributed  
708 to a reduction in the aqueous phase concentration of  $^{14}\text{C}$ -2, 4-DCP in soil solution by 1/5 and 1/12  
709 for SWCNTs and MWCNTs, respectively (Zhou et al., 2013). However, significant inhibitory effects  
710 on the degradation of  $^{14}\text{C}$ -2, 4-DCP when pre-sorbed to CNTs occurred at a CNT concentration of  
711 20  $\text{mg kg}^{-1}$ .

712 These results show that CNT interactions with contaminants within the soil environment  
713 reduced the number of available sorption sites, with their sorptive ability further reduced by CNM

714 aggregation and interaction with soil components such as humic substances, DOM, peptone and  
715 TA, which potentially coat CNTs modifying surface polarity, reducing surface area and hence  
716 reducing HOC sorption capacity as discussed in Section 4.1 (Wang et al., 2008b; Cui et al., 2011;  
717 Zhou et al., 2013). As the adsorption of <sup>14</sup>C-2, 4-DCP to CNTs was reversible, the bioaccessibility of  
718 2,4-DCP was not reduced; however, it may be possible that the indigenous microorganisms were  
719 not able to mineralise desorbed <sup>14</sup>C-2, 4-DCP at the same rate of desorption due to the possible  
720 toxicity effects of CNTs on microbial activity (Zhou et al., 2013). CNTs are therefore potentially  
721 able to increase the persistence of organic pollutants within soil through reducing biodegradation,  
722 with greater effects observed for pre-adsorbed contaminants (Zhou et al., 2013). However, it is  
723 possible to speculate about the environmental relevance of the investigation, as a concentration  
724 of 2000 mg kg<sup>-1</sup> is likely several orders of magnitude higher than could realistically be assumed to  
725 exist (outside of localised 'hot-spots') within the environment (Zhou et al., 2013).

726         Similar results were obtained by Cui et al. (2011). Sediments (20 g) were first amended with  
727 either biochar (100 mg), charcoal (20 mg) or SWCNTs (20 mg), then spiked with phenanthrene  
728 (0.50 mg kg<sup>-1</sup>). The mineralisation of phenanthrene by *Mycobacterium vanbaalenii* PYR1) was  
729 inhibited by 40.3 ± 1.5, 40.5 ± 2.6 and 29.5 ± 3.5% for biochar, charcoal or SWCNTs, respectively.  
730 It was proposed that the larger surface area and pore volume of SWCNTs relative to the other  
731 sorbents was responsible for the reduced phenanthrene mineralisation. However, following the  
732 coating of SWCNTs with either HAs, TAs or peptone, a reduction in phenanthrene sorption  
733 occurred due to reduced pore volumes and surface area, ultimately also reducing the extent to  
734 which sorption to SWCNTs reduced mineralisation (Cui et al., 2011).

735         In addition to the impact of soil types on the impact of CNMs on organic contaminant  
736 sorption, properties of the organic chemicals within soils are also influential in dictating their  
737 interaction with different types of CNMs. Towell et al. (2011) assessed the impact of fullerene  
738 soot (FS), SWCNTs and MWCNTs at 0, 0.05, 0.1 and 0.5% concentrations, on the HPCD  
739 extractability (proven as an indicator of PAH bioaccessibility to soil micro flora (Reid et al., 2000;

740 Doick et al., 2005; Stokes et al., 2005; Rhodes et al., 2008b) and mineralisation of <sup>14</sup>C-  
741 phenanthrene, and HPCD extractability of <sup>14</sup>C-benzo[*a*]pyrene (<sup>14</sup>C-B[*a*]P) in soils over an 80 d  
742 period. Soils were first amended with CNMs, and then spiked with the contaminant. At  
743 concentrations  $\geq 0.05\%$  CNMs, <sup>14</sup>C-phenanthrene mineralisation was significantly inhibited,  
744 suggesting enhanced PAH sorption reduced the aqueous substrate available for microbial  
745 mineralisation (Towell et al., 2011). Differences were also apparent between CNM types, with  
746 SWCNTs generally resulting in greater mineralisation inhibition in relation to MWCNTs and FS  
747 (Towell et al., 2011). However, at a concentration of 0.5% CNMs, <sup>14</sup>C-phenanthrene was  
748 mineralised to a greater extent with SWCNT amendments than FS. This disparity was attributed to  
749 variation in rates of phenanthrene desorption from the solid to aqueous phase, as desorption  
750 hysteresis occurs more commonly with fullerenes than CNTs due to differences in aggregate  
751 structure and availability of sorption sites (Cheng et al., 2005; Yang and Xing, 2007; Towell et al.,  
752 2011). The HPCD extractability of <sup>14</sup>C-phenanthrene was significantly reduced as a result of CNM  
753 amendment in a concentration dependant manner due to increased numbers of sorption sites  
754 resulting in enhanced phenanthrene sorption (Towell et al., 2011). However, while the HPCD  
755 extractability of <sup>14</sup>C-B[*a*]P reduced with increasing concentrations of SWCNTs and MWCNTs, no  
756 significant concentration dependant differences were observed with FS (Towell et al., 2011). The  
757 ability of CNMs to sorb and hence modify the bioaccessibility of HOCs is therefore dependent on  
758 the differences in physicochemical properties of the PAH in relation to the properties of the CNM.  
759 However, the study did not consider possible differences in the toxicity CNMs between particle  
760 types when discussing variations in mineralisation trends.

761       When considering the fraction of contaminants sorbed to CNMs within these investigations,  
762 and the resulting reduced bioavailability, two schools of thought may be adopted; (i) over time  
763 the non-degradable, bound fraction may innocuously degrade (Gevao et al., 2000a), or (ii) the  
764 bound fraction is potentially re-mobilised over long time scales with potential environmental  
765 implications (Gevao et al., 2000b). This draws on the discussion by Semple et al. (2013), in which

766 the significance of distinguishing between bioavailability and bioaccessibility is significant,  
767 particularly when dealing with environmental 'super sorbents' such as CNMs with reference to  
768 remediation of contaminated land and risk assessment. Semple et al. (2004) defined  
769 bioavailability as 'that which is freely available to cross an organism's cellular membrane from the  
770 medium the organism inhabits at a given time', and is considered as a rate of substrate delivery to  
771 cells. While bioaccessibility encompasses this fraction, it additionally extends to those which are  
772 potentially available over time, but are currently chemically or physically removed from the  
773 microorganism (Semple et al., 2004). In other words, it provides a definition of the total extent of  
774 substrate that will be available to cells. Arguably, bioaccessibility is of relatively greater  
775 importance when considering the fate and behaviour of CNM sorbed contaminants, due to the  
776 larger temporal range and lack of implied immediacy. However, under some environmental  
777 conditions, microbial colonisation of CNM agglomerates can occur, with potential implications for  
778 the bioaccessibility of the bound contaminant fraction.

#### 779 *5.4 Microbial sorption and biofilm formation*

780 While the toxicity of CNMs in soil is dependent on their bioaccessibility in addition to  
781 retention of reactivity, if agglomerates of CNMs are present with a reduced cytotoxic nature, it is  
782 conceivable that interstitial gaps in the agglomerate with mesopore dimensions will result in their  
783 increased suitability for the sorption of microorganisms (Agnihotri et al., 2005; Upadhyayula and  
784 Gadhamshetty, 2010). When this is related to the previous discussion of CNM contaminant  
785 sorption and the implications for biodegradation, it is possible to re-consider the lack of  
786 bioaccessibility of CNM sorbed contaminants reported in some studies, and consider their  
787 potential to increase contaminant bioaccessibility in certain situations. Properties of particular  
788 importance when considering CNMs for such applications include: (i) structures with high  
789 porosities readily colonisable by microorganisms; (ii) potential ability to encourage biofilm  
790 formation through offering a buffering capacity and (iii) the ability to adsorb high concentrations

791 of contaminants from bulk solution yet regulate the microbial biodegradation through desorption  
792 (Abu-Salah et al., 1996).

793 Biofilms are groups of well-organised, adjoining cells encapsulated within a matrix of  
794 insoluble, extracellular polymeric substances (EPS) (Morikawa, 2006). EPS encapsulation supports  
795 cell substance and growth through the trapping, binding and dissemination of external nutrients  
796 by charged polysaccharide groups (Cheng et al., 2007), and offers greater protection against  
797 external stresses within the environment relative to those residing in a planktonic state (Pang et  
798 al., 2005). Materials that allow a high degree of bacterial colonisation and possibly biofilm  
799 formation are potentially suited to facilitating biodegradation (Upadhyayula and Gadhamshetty,  
800 2010), which is typically most effective when microorganisms are in biofilm state relative to  
801 planktonic, due to greater bioavailability, protection and adaptability to toxic conditions and  
802 hence more rapid pollutant degradation (Singh and Cameotra, 2004; Singh et al., 2006).  
803 Furthermore, bacterial colonisation may stabilise nanoparticle aggregates, as polysaccharides  
804 such as those generated by bacteria, have been observed to significantly increase the aggregation  
805 of C<sub>60</sub> fullerene, reducing particle mobility within the environment (Espinasse et al., 2007).

806 Upadhyayula and Gadhamshetty (2010) conducted hypothetical calculations to determine  
807 the quantity of cells that an agglomerate of CNTs could potentially sorb. The dimensions of a  
808 typical bacterium such as *Shewanella oneidensis* (*S. oneidensis*) are 2 µm in height with a radius of  
809 0.5 µm, resulting in a surface area of 7.85 x10<sup>-12</sup> m<sup>2</sup>. Assuming that 10% of the surface area of 0.1g  
810 CNTs added to media was available for bacterial sorption, the CNTs would be able to sorb 3.18  
811 E+13 *S. oneidensis* cells (Upadhyayula and Gadhamshetty, 2010). Furthermore, Upadhyayula et al.  
812 (2009) confirmed that the adsorptive capacity of nanotubes for the bacterial strain *Bacillus subtilis*  
813 to be 37 times greater than the capacity of activated carbon; however, this may vary depending  
814 upon pore volumes and surface area, which are key determinants of immobilisation capacity  
815 (Upadhyayula and Gadhamshetty, 2010). Given these parameters, it is conceivable that biofilms  
816 could develop on CNM aggregates given sufficient pore volumes and diminished CNM reactivity.



817           When the potential for biofilm development on CNMs is considered in relation to their HOC  
818 sorptive ability and aggregation within soils, it has been suggested that CNMs may be useful for  
819 enhancing biodegradation of organic pollutants that cannot be easily concentrated. With CNM  
820 aggregates behaving as an organic chemical collector and accumulator, biofilm development on  
821 CNMs potentially increases the bioavailability/bioaccessibility of the contaminant (Yang et al.,  
822 2006b). Given adequate reversibility of organic compound adsorption and limited desorption  
823 hysteresis, sorption of bacterial cells to the surface of CNM aggregates may shorten the diffusion  
824 distance, facilitating the utilisation of the sorbed organic compound by the bacteria. This is well  
825 illustrated by Yan et al. (2004), who studied the removal efficiency of microcystins (MCs) toxins  
826 from solution by *Ralstonia solanacearum* bacteria (Gram-negative cells which are able to readily  
827 coalesce on fibrous material) immobilised as a biofilm on a nontoxic form of CNTs. Their results  
828 showed that the removal efficiencies of MCs were 20% greater by CNT biological composites than  
829 either CNTs or bacteria alone (Yan et al., 2004). The findings were explained through absorption  
830 of large amounts of MCs and *R. solanacearum* by CNTs, resulting in a concerted biodegradation  
831 reaction (Yan et al., 2004). In a similar investigation, Kanepalli and Donna (2006) used CNT-  
832 bacteria nanocomposites to assess the bioremediation of highly persistent trichloroethylene (TCE)  
833 in groundwater. The study revealed that TCE instantly sorbed to bacteria-nanocomposites, which  
834 was later released to bacteria that were immobilised on the surface and metabolised.

835           Xia et al. (2013) studied the bioavailability and desorption (Tenax TA) of <sup>14</sup>C phenanthrene  
836 aged over 60 d with four different MWCNTs with varying surface areas in aqueous solution.  
837 MWCNTs significantly ( $P<0.05$ ) reduced the mineralisation of phenanthrene in accordance with  
838 their properties, with particles possessing larger specific surface areas together with large meso-  
839 and micro-pore volumes resulting in the lowest mineralisation efficiencies. Bacteria were also  
840 observed to colonise the surface of MWCNT aggregates, proportional to the quantity of  
841 phenanthrene desorbed through Tenax TA extractions (Xia et al., 2013). Although slight changes  
842 to the physical appearance of the bacteria were observed when sorbed to MWCNT aggregates,

843 potentially indicating a toxicity effect, the ability of the cells to metabolised phenanthrene sorbed  
844 to low surface area particles may not have been significantly reduced (Xia et al., 2013). However,  
845 the lack of a control sample in which the metabolism of cells under conditions devoid of CNMs  
846 was assessed, limited the ability of the paper to determine the overall impact of MWCNT  
847 aggregates on phenanthrene mineralisation.

848       Very little information is available on how CNMs act within soil matrices, especially in relation  
849 to their adsorption to organic fractions, organic pollutants and their subsequent toxicity (Dinesh  
850 et al., 2012). With an angelus sorbents such as black carbon (BC), elevated mineralisation of a  
851 phenanthrene substrate has been observed as a direct result of BC addition to soil, which was  
852 tentatively attributed to microbial sorption and utilisation of phenanthrene from the sorbed  
853 phase (Rhodes et al., 2008a; Rhodes et al., 2012). Only one study has identified an increase in  
854 contaminant mineralisation in soils following the addition of CNMs. Xia et al. (2010) studied  
855 phenanthrene biodegradation and desorption characteristics (using XAD-2) in 21-40 day aged  
856 MWCNT-amended soils relative to soils amended with wood char and black carbon. Following  
857 each ageing interval, *Agrobacterium* (the degrading inoculum) was added to the soil, and the  
858 contaminant degradation efficiency measured. After 28 and 40 days ageing, the degradation  
859 efficiency in MWCNT-amended soils was 54.2% and 24.6%, respectively; wood char amended  
860 73.5% and 25.1%, respectively and black carbon amended 83.8% and 38.3%, respectively. Thus a  
861 reduction in bioavailability of contaminants sorbed to each of the sorbents with increasing soil  
862 contact time is observed (Xia et al., 2010), together with the relatively low bioavailability of  
863 contaminants sorbed to MWCNTs relative to other environmental sorbents. Desorption studies  
864 identified similar residual concentrations of phenanthrene; however, during rapid stages of  
865 degradation, desorption rates were found to under-predict the rate of degradation (Xia et al.,  
866 2010). This potentially suggests that for each of the sorbents, phenanthrene was available to  
867 bacteria either through the promotion of desorption or direct access (Xia et al., 2010).

868           Given the discussion above, it is possible to consider an additional factor to those proposed by  
869 Kretzschmar et al. (1999) in Section 4, to determine the significance of contaminant facilitated  
870 transport by CNMs. If the CNM sorbed contaminant is available to the cells through utilisation  
871 from the sorbed phase, the importance of desorption of sorbed compounds from CNMs during  
872 transport is reduced. It is therefore proposed that incorporation of a fifth factor, ‘the  
873 bioavailability and bioaccessibility of CNM sorbed contaminants to microorganisms from the solid  
874 phase’, may be appropriate, as inferring bioaccessibility through desorption investigations may  
875 lead to incorrect assumptions. However, substantially more work is required to identify the exact  
876 mechanism involved in these findings, and the specific conditions under which contaminant and  
877 microbial sorption to CNMs could potentially result in toxicity from the CNM itself, from the  
878 sorbed contaminant or both (Nowack and Bucheli, 2007). It is also possible that under some  
879 environmental conditions, rapid desorption or excessive bioavailability of sorbed contaminants  
880 may shock load sorbed bacteria and prove toxic (Upadhyayula and Gadhamshetty, 2010).  
881 Biodegradation of contaminants sorbed to CNMs therefore still requires substantial investigation  
882 into specific combinations of pollutants and microorganisms (Upadhyayula and Gadhamshetty,  
883 2010), to determine whether the bioaccessibility of sorbed contaminants is either increased or  
884 decreased, and if the addition of CNMs will increase the mobility of contaminants in the  
885 environment. The general paucity of knowledge regarding the duration for which contaminants  
886 will remain sorbed to CNMs requires addressing to determine the long-term stability of  
887 contaminants sorbed to different nanoparticle types. Furthermore, the extent to which CNMs  
888 influence the transformation residues of HOCs in soils such as bound residues formed during  
889 organic pollution degradation in soil is unknown (Barriuso et al., 2008; Shan et al., 2011; Zhou et  
890 al., 2013).

## 891 **6. Summary and conclusions**

892           The complex and dynamic nature of both soil environments and CNM physicochemical  
893 properties generates enormous uncertainty in attempting to predict their behaviour and impact

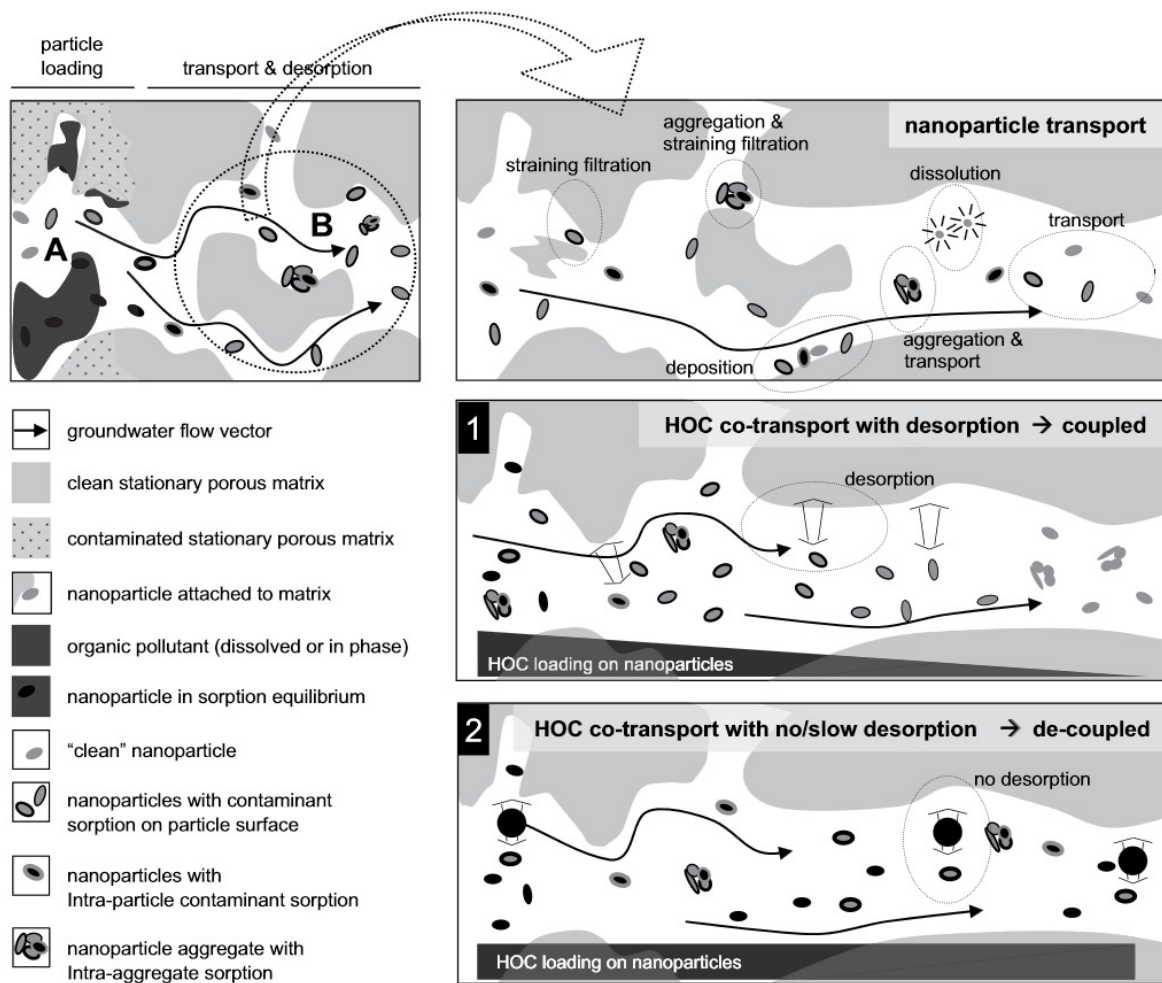
894 on contaminant sorption, sequestration and transport as well as microbial interactions. This  
895 review argues that the fate and behaviour of CNMs in soils is influenced by multiple parameters  
896 such as the type and quantity of SOM, the type of clay particles present, the dominant charge  
897 characteristics of the matrix as dictated by the soil inorganic fraction, together with properties of  
898 the CNM, each of which is heavily influenced by pH and ionic strength. In addition, to a small  
899 extent, biological activity has been shown to modify carbon nanomaterial fate. However,  
900 presently no research has been conducted into the manner in which each these factors interact  
901 and collaboratively influence the fate and behaviour CNMs in real environmental scenarios, and  
902 significantly more research is required.

903 The extent to which CNMs are able to modify the behaviour of contaminants in soils and  
904 facilitate their transport is dependent on the CNM concentration, the properties of SOM,  
905 molecular weight of the HOC and interaction of the CNM with the HOC before the addition to  
906 soils. When present in sufficient concentrations, CNMs have the ability to facilitate the transport  
907 of co-existing contaminants such as PAHs to a greater extent than naturally occurring colloids  
908 such as DOM, the extent of which is dependent on the physicochemical properties of the  
909 contaminant, CNM functionalization status, aggregation size and method of preparation. Further  
910 work derived from experimental research is needed to address the lack of data relating to the  
911 transport of CNMs through soils of different properties. Additionally, CNM-HOC desorption  
912 kinetics within soils require defining, as this presently limits our understanding of the significance  
913 CNM facilitated transport.

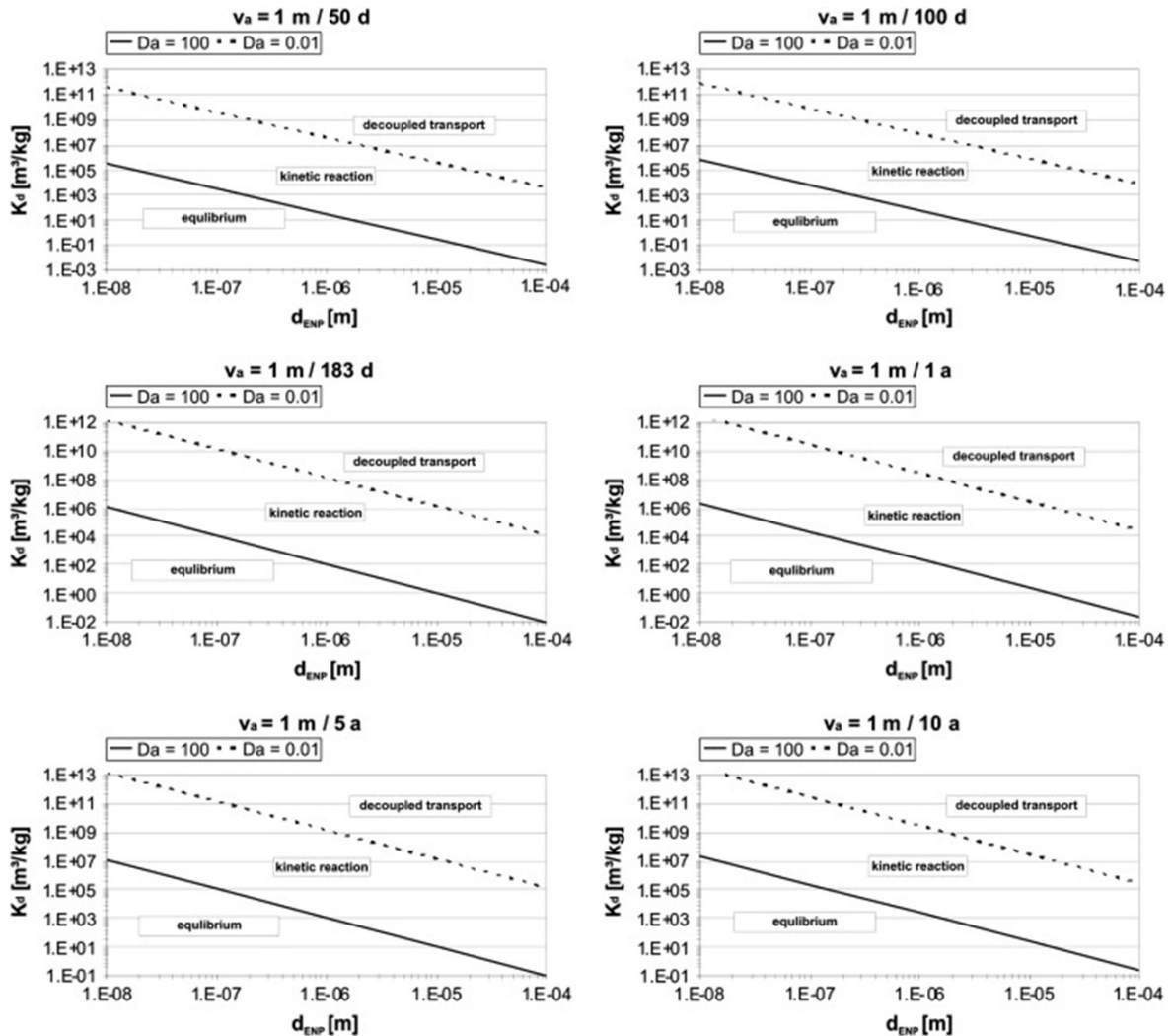
914 Finally, CNMs are undoubtedly efficient sorbents for a range of HOCs. However, while a  
915 reduction in bioaccessibility of contaminants in soils has been demonstrated (Towell et al., 2011),  
916 possibly indicating to uses as agents to land reduce bioaccessibility of contaminants, information  
917 regarding sorption stability together with their potential to increase contaminant mobilisation  
918 and other secondary effects are as yet too poorly developed to fully anticipate the possible  
919 environmental impact. To determine the behaviour of CNMs within soils, it is concluded that no

920 one set of environmental or CNM characteristics can be viewed in isolation. Hence, given the  
921 diverse array of variables, it is argued that risk-assessment of CNMs within the soil environment  
922 should be conducted on a case-by-case basis. Detailed analysis of other environmental  
923 compartments in which CNMs can potentially accumulate such as sediments, should also be  
924 considered.

925



927 **Figure 1.** ‘Worst case scenario’ processes by which CNMs may facilitate the transport of HOCs.  
 928 Top left panel: (A) HOC equilibrates with CNM, and is (B) transported. Top right panel shows the  
 929 processes by which CNMs may be transported. The centre right panel (1) show the transport and  
 930 rapid desorption of HOCs from CNMs. Equilibrium is achieved between the liquid phase, CNM and  
 931 matrix. (2) shows slow desorption kinetics, with no desorption from the CNM (Hofmann and von  
 932 der Kammer, 2009). Re-printed with permission from Elsevier, © 2014.



934

935 **Figure 2.** Simulation of diffusion limited desorption using of pore water velocities ( $v_a$ ) between 1  
 936 m/50 d to 1 m/10m/y. The solid line represents the Damköhler number of 100 (representing  
 937 equilibrium transport above which the HOC will equilibrate between the CNM and soil matrix),  
 938 the dashed line indicates a Damköhler number of 0.01 (decoupled transport below which HOC  
 939 desorption will not occur within the timeframe of transport). If Damköhler numbers are  $< 100$  or  
 940  $> 0.01$ , kinetics of sorption should be considered in transport models (Hofmann and von der  
 941 Kammer, 2009). Re-printed with permission from Elsevier, © 2014.

Table 1. Recent methods used to detect CNMs in complex environmental matrices.

Author	Method of Detection	CNM Type Used	Matrix Characteristics	Results	Notable Advantages	Notable Disadvantages
Doudrick et al. (2012)	Separation of organic and elemental carbon using thermal optical transmittance/reflectance	SWCNTs and MWCNTs	Sediment		No interference from naturally occurring elemental carbon with CNTs that combusted at high temperatures	Interference from elemental carbon with CNTs that combusted at low temperatures
Plata et al. (2012)	Thermogravimetric analysis coupled with mass spectrometry	SWCNTs	Sediment	Detection limit of $100 \mu\text{g g}^{-1}$	Capable of distinguishing between naturally occurring soot and manufactured CNMs	
Schierz et al. (2012)	Near-Infrared fluorescence spectroscopy	SWCNTs	Sediment	$62 \text{ ng g}^{-1}$	Able to differentiate SWCNTs from naturally occurring soot	
Sobek and Bucheli (2009)	Chemothermal oxidation at $375 \text{ }^\circ\text{C}$	SWCNTs, MWCNTs	Clay (vertisol) & marine sediment	Highly variable detection of CNTs depending on CNT structure and complexity of matrix	Able to isolate CNTs from matrix	Unable to distinguish CNTs from naturally occurring soot



943 **References**

- 944 Abu-Salah, K., Shelef, G., Levanon, D., Armon, R. & Dosoretz, C. G. 1996. Microbial degradation of  
 945 aromatic and polyaromatic toxic compounds adsorbed on powdered activated carbon.  
 946 *Journal of Biotechnology*, 51, 265-272.
- 947 Agnihotri, S., Mota, J. P. B., Rostam-Abadi, M. & Rood, M. J. 2005. Structural characterization of  
 948 single-walled carbon nanotube bundles by experiment and molecular simulation.  
 949 *Langmuir*, 21, 896-904.
- 950 Allen, B. L., Kichambare, P. D., Gou, P., Vlasova, I. I., Kapralov, A. A., Konduru, N., Kagan, V. E. &  
 951 Star, A. 2008. Biodegradation of Single-Walled Carbon Nanotubes through Enzymatic  
 952 Catalysis. *Nano Letters*, 8, 3899-3903.
- 953 Allen, B. L., Kotchey, G. P., Chen, Y., Yanamala, N. V. K., Klein-Seetharaman, J., Kagan, V. E. & Star,  
 954 A. 2009. Mechanistic Investigations of Horseradish Peroxidase-Catalyzed Degradation of  
 955 Single-Walled Carbon Nanotubes. *Journal of the American Chemical Society*, 131, 17194-  
 956 17205.
- 957 Almecija, D., Blond, D., Sader, J. E., Coleman, J. N. & Boland, J. J. 2009. Mechanical properties of  
 958 individual electrospun polymer-nanotube composite nanofibers. *Carbon*, 47, 2253-2258.
- 959 Aruguete, D. M. & Hochella, M. F. 2010. Bacteria-nanoparticle interactions and their  
 960 environmental implications. *Environmental Chemistry*, 7, 3-9.
- 961 Barriuso, E., Benoit, P. & Dubus, I. G. 2008. Formation of pesticide nonextractable (bound)  
 962 residues in soil: Magnitude, controlling factors and reversibility. *Environmental Science &  
 963 Technology*, 42, 1845-1854.
- 964 Bold, S., Kraft, S., Grathwohl, P. & Liedl, R. 2003. Sorption/desorption kinetics of contaminants on  
 965 mobile particles: Modeling and experimental evidence. *Water Resources Research*, 39,  
 966 1329.
- 967 Campbell, E. E. B. & Rohmund, F. 2000. Fullerene reactions. *Rep. Prog. Phys.*, 63, 1061.
- 968 Carter, M. C. & Weber, W. J. 1994. Modeling Adsorption of TCE by Activated Carbon Preloaded by  
 969 Background Organic Matter. *Environmental Science & Technology*, 28, 614-623.
- 970 Cebulska-Wasilewska, A., Pawlyk, I., Panek, A., Wiecheć, A., Kalina, I., Popov, T., Georgieva, T. &  
 971 Farmer, P. B. 2007. Exposure to environmental polycyclic aromatic hydrocarbons:  
 972 Influences on cellular susceptibility to DNA damage (sampling Košice and Sofia). *Mutation  
 973 Research*, 620, 145-154.
- 974 Chae, S.-R., Xiao, Y., Lin, S., Noeiaghahi, T., Kim, J.-O. & Wiesner, M. R. 2012. Effects of humic acid  
 975 and electrolytes on photocatalytic reactivity and transport of carbon nanoparticle  
 976 aggregates in water. *Water Research*, 46, 4053-4062.
- 977 Chappell, M. A., George, A. J., Dontsova, K. M., Porter, B. E., Price, C. L., Zhou, P., Morikawa, E.,  
 978 Kennedy, A. J. & Steevens, J. A. 2009. Surfactive stabilization of multi-walled carbon  
 979 nanotube dispersions with dissolved humic substances. *Environmental Pollution*, 157,  
 980 1081-1087.
- 981 Chen, J., Chen, W. & Zhu, D. 2008. Adsorption of Nonionic Aromatic Compounds to Single-Walled  
 982 Carbon Nanotubes: Effects of Aqueous Solution Chemistry. *Environmental Science &  
 983 Technology*, 42, 7225-7230.
- 984 Chen, K. L. & Elimelech, M. 2008. Interaction of Fullerene (C60) Nanoparticles with Humic Acid  
 985 and Alginate Coated Silica Surfaces: Measurements, Mechanisms, and Environmental  
 986 Implications. *Environmental Science & Technology*, 42, 7607-7614.
- 987 Chen, K. L. & Elimelech, M. 2009. Relating Colloidal Stability of Fullerene (C60) Nanoparticles to  
 988 Nanoparticle Charge and Electrokinetic Properties. *Environmental Science & Technology*,  
 989 43, 7270-7276.
- 990 Chen, W., Duan, L. & Zhu, D. 2007. Adsorption of Polar and Nonpolar Organic Chemicals to Carbon  
 991 Nanotubes. *Environmental Science & Technology*, 41, 8295-8300.
- 992 Chen, Z., Yadghar, A. M., Zhao, L. & Mi, Z. 2011. A review of environmental effects and  
 993 management of nanomaterials. *Toxicological & Environmental Chemistry*, 93, 1227-1250.

- 994 Cheng, G., Zhang, Z., Chen, S., Bryers, J. D. & Jiang, S. 2007. Inhibition of bacterial adhesion and  
995 biofilm formation on zwitterionic surfaces. *Biomaterials*, 28, 4192-4199.
- 996 Cheng, X., Kan, A. T. & Tomson, M. B. 2005. Uptake and Sequestration of Naphthalene and 1,2-  
997 Dichlorobenzene by C60. *Journal of Nanoparticle Research*, 7, 555-567.
- 998 Chibowski, E., Espinosa-Jiménez, M., Ontiveros-Ortega, A. & Giménez-Martin, E. 1998. Surface  
999 Free Energy, Adsorption and Zeta Potential in Leacril/Tannic Acid System. *Langmuir*, 14,  
1000 5237-5244.
- 1001 Chijiwa, T., Arai, T., Sugai, T., Shinohara, H., Kumazawa, M., Takano, M. & Kawakami, S. 1999.  
1002 Fullerenes found in the Permo-Triassic mass extinction period. *Geophysical Research  
1003 Letters*, 26, 767-770.
- 1004 Choi, H. & Yavuz Corapcioglu, M. 1997. Transport of a non-volatile contaminant in unsaturated  
1005 porous media in the presence of colloids. *Journal of Contaminant Hydrology*, 25, 299-324.
- 1006 Chung, H., Son, Y., Yoon, T. K., Kim, S. & Kim, W. 2011. The effect of multi-walled carbon  
1007 nanotubes on soil microbial activity. *Ecotoxicology and Environmental Safety*, 74, 569-575.
- 1008 Colvin, V. L. 2003. The potential environmental impact of engineered nanomaterials. *Nature  
1009 Biotechnology*, 21, 1166-1170.
- 1010 Corapcioglu, M. Y., Jiang, S. & Kim, S.-H. 1999. Comparison of Kinetic and Hybrid-Equilibrium  
1011 Models Simulating Colloid-Facilitated Contaminant Transport in Porous Media. *Transport  
1012 in Porous Media*, 36, 373-390.
- 1013 Cornelissen, G., Van Noort, P. C. M. & Govers, H. a. J. 1997. Desorption kinetics of chlorobenzenes,  
1014 polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction  
1015 with Tenax® and effects of contact time and solute hydrophobicity. *Environmental  
1016 Toxicology and Chemistry*, 16, 1351-1357.
- 1017 Cui, X. Y., Jia, F., Chen, Y. X. & Gan, J. 2011. Influence of single-walled carbon nanotubes on  
1018 microbial availability of phenanthrene in sediment. *Ecotoxicology*, 20, 1277-1285.
- 1019 Darlington, T. K., Neigh, A. M., Spencer, M. T., Guyen, O. T. N. & Oldenburg, S. J. 2009.  
1020 Nanoparticle characteristics affecting environmental fate and transport through soil.  
1021 *Environmental Toxicology and Chemistry*, 28, 1191-1199.
- 1022 De Jonge, L. W., Kjaergaard, C. & Moldrup, P. 2004. Colloids and Colloid-Facilitated Transport of  
1023 Contaminants in Soils: An Introduction. *Vadose Zone Journal*, 3, 321-325.
- 1024 Debnath, S., Cheng, Q., Hedderman, T. G. & Byrne, H. J. 2008. An experimental study of the  
1025 interaction between single walled carbon nanotubes and polycyclic aromatic  
1026 hydrocarbons. *Physica Status Solidi (B)*, 245, 1961-1963.
- 1027 Dinesh, R., Anandaraj, M., Srinivasan, V. & Hamza, S. 2012. Engineered nanoparticles in the soil  
1028 and their potential implications to microbial activity. *Geoderma*, 173-174, 19-27.
- 1029 Doick, K. J., Dew, N. M. & Semple, K. T. 2005. Linking Catabolism to Cyclodextrin Extractability:  
1030 Determination of the Microbial Availability of PAHs in Soil. *Environmental Science &  
1031 Technology*, 39, 8858-8864.
- 1032 Doudrick, K., Herckes, P. & Westerhoff, P. 2012. Detection of Carbon Nanotubes in Environmental  
1033 Matrices Using Programmed Thermal Analysis. *Environmental Science & Technology*, 46,  
1034 12246-12253.
- 1035 Ekelund, F., Olsson, S. & Johansen, A. 2003. Changes in the succession and diversity of protozoan  
1036 and microbial populations in soil spiked with a range of copper concentrations. *Soil  
1037 Biology & Biochemistry*, 35, 1507-1516.
- 1038 Espinasse, B., Hotze, E. M. & Wiesner, M. R. 2007. Transport and Retention of Colloidal  
1039 Aggregates of C60 in Porous Media: Effects of Organic Macromolecules, Ionic  
1040 Composition, and Preparation Method. *Environmental Science & Technology*, 41, 7396-  
1041 7402.
- 1042 Esquivel, E. V. & Murr, L. E. 2004. A TEM analysis of nanoparticulates in a Polar ice core. *Materials  
1043 Characterization*, 52, 15-25.
- 1044 Finkel, M., Liedl, R. & Teutsch, G. 1998. Modelling surfactant-enhanced remediation of polycyclic  
1045 aromatic hydrocarbons. *Environmental Modelling & Software*, 14, 203-211.

1046 Gai, K., Shi, B., Yan, X. & Wang, D. 2011. Effect of Dispersion on Adsorption of Atrazine by  
1047 Aqueous Suspensions of Fullerenes. *Environmental Science & Technology*, 45, 5959-5965.

1048 Gevao, B., Mordaunt, C., Semple, K. T., Pearce, T. G. & Jones, K. C. 2000a. Bioavailability of  
1049 Nonextractable (Bound) Pesticide Residues to Earthworms. *Environmental Science &  
1050 Technology*, 35, 501-507.

1051 Gevao, B., Semple, K. T. & Jones, K. C. 2000b. Bound pesticide residues in soils: a review.  
1052 *Environmental Pollution*, 108, 3-14.

1053 Giles, J. 2006. Top five in physics. *Nature*, 441, 265.

1054 Gottschalk, F., Sonderer, T., Scholz, R. W. & Nowack, B. 2009. Modeled Environmental  
1055 Concentrations of Engineered Nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT, Fullerenes) for  
1056 Different Regions. *Environmental Science & Technology*, 43, 9216-9222.

1057 Gottschalk, F., Sonderer, T., Scholz, R. W. & Nowack, B. 2010. Possibilities and limitations of  
1058 modeling environmental exposure to engineered nanomaterials by probabilistic material  
1059 flow analysis. *Environmental Toxicology and Chemistry*, 29, 1036-1048.

1060 Han, Z., Zhang, F., Lin, D. & Xing, B. 2008. Clay Minerals Affect the Stability of Surfactant-  
1061 Facilitated Carbon Nanotube Suspensions. *Environmental Science & Technology*, 42, 6869-  
1062 6875.

1063 Heymann, D., Chibante, L. P., Brooks, R. R., Wolbach, W. S. & Smalley, R. E. 1994. Fullerenes in the  
1064 Cretaceous-Tertiary Boundary-Layer. *Science*, 265, 645-647.

1065 Hofmann, T. & Von Der Kammer, F. 2009. Estimating the relevance of engineered carbonaceous  
1066 nanoparticle facilitated transport of hydrophobic organic contaminants in porous media.  
1067 *Environmental Pollution*, 157, 1117-1126.

1068 Holden, P. A., Klaessig, F., Turco, R. F., Priester, J. H., Rico, C. M., Avila-Arias, H., Mortimer, M.,  
1069 Pacpaco, K. & Gardea-Torresdey, J. L. 2014. Evaluation of Exposure Concentrations Used  
1070 in Assessing Manufactured Nanomaterial Environmental Hazards: Are They Relevant?  
1071 *Environmental Science & Technology*, In Press.

1072 Hou, W.-C. & Jafvert, C. T. 2008. Photochemical Transformation of Aqueous C<sub>60</sub> Clusters in  
1073 Sunlight. *Environmental Science & Technology*, 43, 362-367.

1074 Hou, W.-C. & Jafvert, C. T. 2009. Photochemistry of Aqueous C<sub>60</sub> Clusters: Evidence of 1O<sub>2</sub>  
1075 Formation and its Role in Mediating C<sub>60</sub> Phototransformation. *Environmental Science &  
1076 Technology*, 43, 5257-5262.

1077 Hu, H., Yu, A., Kim, E., Zhao, B., Itkis, M. E., Bekyarova, E. & Haddon, R. C. 2005. Influence of the  
1078 Zeta Potential on the Dispersability and Purification of Single-Walled Carbon Nanotubes.  
1079 *The Journal of Physical Chemistry B*, 109, 11520-11524.

1080 Hyung, H., Fortner, J. D., Hughes, J. B. & Kim, J.-H. 2006. Natural Organic Matter Stabilizes Carbon  
1081 Nanotubes in the Aqueous Phase. *Environmental Science & Technology*, 41, 179-184.

1082 Hyung, H. & Kim, J.-H. 2008. Natural Organic Matter (NOM) Adsorption to Multi-Walled Carbon  
1083 Nanotubes: Effect of NOM Characteristics and Water Quality Parameters. *Environmental  
1084 Science & Technology*, 42, 4416-4421.

1085 Ibaraki, M. & Sudicky, E. A. 1995. Colloid-facilitated contaminant transport in discretely fractured  
1086 porous media: 1. Numerical formulation and sensitivity analysis. *Water Resources  
1087 Research*, 31, 2945-2960.

1088 Isaacson, C., Zhang, W., Powell, T., Ma, X. & Bouchard, D. 2011. Temporal Changes in Aqu/C<sub>60</sub>  
1089 Physical-Chemical, Deposition, and Transport Characteristics in Aqueous Systems.  
1090 *Environmental Science & Technology*, 45, 5170-5177.

1091 Jafar, G. & Hamzeh, G. 2013. Ecotoxicity of Nanomaterials in Soil. *Annals of Biological Research*, 4,  
1092 86-92.

1093 Jaisi, D. P. & Elimelech, M. 2009. Single-Walled Carbon Nanotubes Exhibit Limited Transport in Soil  
1094 Columns. *Environmental Science & Technology*, 43, 9161-9166.

1095 Jennings, A. A. & Kirkner, D. J. 1984. Instantaneous Equilibrium Approximation Analysis. *Journal of  
1096 Hydraulic Engineering*, 110, 1700-1717.

- 1097 Johansen, A., Pedersen, A. L., Jensen, K. A., Karlson, U., Hansen, B. M., Scott-Fordsmand, J. J. &  
1098 Winding, A. 2008. Effects of C60 fullerene nanoparticles on soil bacteria and protozoans.  
1099 *Environmental Toxicology and Chemistry*, 27, 1895-1903.
- 1100 Kan, A. T. & Tomson, M. B. 1990. Ground water transport of hydrophobic organic compounds in  
1101 the presence of dissolved organic matter. *Environmental Toxicology and Chemistry*, 9,  
1102 253-263.
- 1103 Kanepalli, S. & Donna, F. E. 2006. Enhancing the remediation of trichloroethene (TCE) using  
1104 double-walled carbon nanotubes (DWCNT). United States Geological Survey.
- 1105 Kang, S., Pinault, M., Pfefferle, L. D. & Elimelech, M. 2007. Single-Walled Carbon Nanotubes  
1106 Exhibit Strong Antimicrobial Activity. *Langmuir*, 23, 8670-8673.
- 1107 Köhler, A. R., Som, C., Helland, A. & Gottschalk, F. 2008. Studying the potential release of carbon  
1108 nanotubes throughout the application life cycle. *Journal of Cleaner Production*, 16, 927-  
1109 937.
- 1110 Kretzschmar, R., Borkovec, M., Grolimund, D. & Elimelech, M. 1999. Mobile Subsurface Colloids  
1111 and Their Role in Contaminant Transport. In: Donald, L. S. (ed.) *Advances in Agronomy*.  
1112 Academic Press.
- 1113 Kuznar, Z. A. & Elimelech, M. 2004. Adhesion Kinetics of Viable *Cryptosporidium parvum* Oocysts  
1114 to Quartz Surfaces. *Environmental Science & Technology*, 38, 6839-6845.
- 1115 Kwon, J.-H. 2012. Destabilization of aqueous colloidal C60 nanoparticles in the presence of various  
1116 organic matter. *CLEAN – Soil, Air, Water*, 40, 472-478.
- 1117 Lead, J. R. & Wilkinson, K. J. 2006. Aquatic colloids and nanoparticles: Current knowledge and  
1118 future trends. *Environmental Chemistry*, 3, 159-171.
- 1119 Lee, J., Cho, M., Fortner, J. D., Hughes, J. B. & Kim, J.-H. 2009. Transformation of Aggregated C60  
1120 in the Aqueous Phase by UV Irradiation. *Environmental Science & Technology*, 43, 4878-  
1121 4883.
- 1122 Lee, M. C., Snoeyink, V. L. & Crittenden, J. C. 1981. Activated carbon adsorption of humic  
1123 substances. *American Water Works Association*, 73, 440-446.
- 1124 Lerman, I., Chen, Y. & Chefetz, B. 2013. Adsorption of Contaminants of Emerging Concern by  
1125 Carbon Nanotubes: Influence of Dissolved Organic Matter. In: Xu, J., Wu, J. & He, Y. (eds.)  
1126 *Functions of Natural Organic Matter in Changing Environment*. Springer Netherlands.
- 1127 Li, D., Lyon, D. Y., Li, Q. & Alvarez, P. J. J. 2008. Effect of soil sorption and aquatic natural organic  
1128 matter on the antibacterial activity of a fullerene water suspension. *Environmental*  
1129 *Toxicology and Chemistry*, 27, 1888-1894.
- 1130 Li, Q., Xie, B., Hwang, Y. S. & Xu, Y. 2009. Kinetics of C60 Fullerene Dispersion in Water Enhanced  
1131 by Natural Organic Matter and Sunlight. *Environmental Science & Technology*, 43, 3574-  
1132 3579.
- 1133 Li, S. 2012. *A study of environmental fate and application of commercially available carbon*  
1134 *nanotubes*. Doctor of Philosophy Thesis, Texas Tech University.
- 1135 Li, W., Zhu, X., He, Y., Xing, B., Xu, J. & Brookes, P. C. 2013. Enhancement of water solubility and  
1136 mobility of phenanthrene by natural soil nanoparticles. *Environmental Pollution*, 176, 228-  
1137 233.
- 1138 Li, W. J. & Liang, W. J. 2007. Loss of characteristic absorption bands of C60 conjugation systems in  
1139 the addition with aliphatic amines. *Spectrochimica Acta Part A: Molecular and*  
1140 *Biomolecular Spectroscopy*, 67, 1346-1350.
- 1141 Lin, D. & Xing, B. 2008. Tannic Acid Adsorption and Its Role for Stabilizing Carbon Nanotube  
1142 Suspensions. *Environmental Science & Technology*, 42, 5917-5923.
- 1143 Liu, C., Fan, Y. Y., Liu, M., Cong, H. T., Cheng, H. M. & Dresselhaus, M. S. 1999. Hydrogen Storage in  
1144 Single-Walled Carbon Nanotubes at Room Temperature. *Science*, 286, 1127-1129.
- 1145 Lou, L., Luo, L., Wang, W., Xu, X., Hou, J., Xun, B. & Chen, Y. 2011. Impact of black carbon  
1146 originated from fly ash and soot on the toxicity of pentachlorophenol in sediment. *Journal*  
1147 *of Hazardous Materials*, 190, 474-479.
- 1148 Lubick, N. 2008. Risks of Nanotechnology Remain Uncertain. *Environmental Science & Technology*,  
1149 42, 1821-1824.

- 1150 Lucafò, M., Pacor, S., Fabbro, C., Da Ros, T., Zorzet, S., Prato, M. & Sava, G. 2012. Study of a  
 1151 potential drug delivery system based on carbon nanoparticles: effects of fullerene  
 1152 derivatives in MCF7 mammary carcinoma cells. *Journal of Nanoparticle Research*, 14, 1-  
 1153 13.
- 1154 Mauter, M. S. & Elimelech, M. 2008. Environmental Applications of Carbon-Based Nanomaterials.  
 1155 *Environmental Science & Technology*, 42, 5843-5859.
- 1156 Mehmannaavaz, R., Prasher, S. O. & Ahmad, D. 2001. Cell surface properties of rhizobial strains  
 1157 isolated from soils contaminated with hydrocarbons: hydrophobicity and adhesion to  
 1158 sandy soil. *Process Biochemistry*, 36, 683-688.
- 1159 Menzie, C. A., Potocki, B. B. & Santodonato, J. 1992. Exposure to carcinogenic PAHs in the  
 1160 environment. *Environmental Science & Technology*, 26, 1278-1284.
- 1161 Mohanty, B., Anita, K. V., Claesson, P. & Bohidar, H. B. 2007. Physical and anti-microbial  
 1162 characteristics of carbon nanoparticles prepared from lamp soot. *Nanotechnology*, 18,  
 1163 445102.
- 1164 Morikawa, M. 2006. Beneficial biofilm formation by industrial bacteria *Bacillus subtilis* and related  
 1165 species. *Journal of Bioscience and Bioengineering*, 101, 1-8.
- 1166 Mueller, N. C. & Nowack, B. 2008. Exposure Modeling of Engineered Nanoparticles in the  
 1167 Environment. *Environmental Science & Technology*, 42, 4447-4453.
- 1168 Navarro, E., Baun, A., Behra, R., Hartmann, N., Filser, J., Miao, A.-J., Quigg, A., Santschi, P. & Sigg,  
 1169 L. 2008. Environmental behavior and ecotoxicity of engineered nanoparticles to algae,  
 1170 plants, and fungi. *Ecotoxicology*, 17, 372-386.
- 1171 Neal, A. L. 2008. What can be inferred from bacterium–nanoparticle interactions about the  
 1172 potential consequences of environmental exposure to nanoparticles? *Ecotoxicology*, 17,  
 1173 362-371.
- 1174 Nowack, B. & Bucheli, T. D. 2007. Occurrence, behavior and effects of nanoparticles in the  
 1175 environment. *Environmental Pollution*, 150, 5-22.
- 1176 Pan, B. & Xing, B. 2008. Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes.  
 1177 *Environmental Science & Technology*, 42, 9005-9013.
- 1178 Pan, B. & Xing, B. 2010. Manufactured nanoparticles and their sorption of organic chemicals.  
 1179 *Advances in Agronomy*, 108, 137-181.
- 1180 Pan, B. & Xing, B. 2012. Applications and implications of manufactured nanoparticles in soils: a  
 1181 review. *European Journal of Soil Science*, 63, 437-456.
- 1182 Pang, C. M., Hong, P., Guo, H. & Liu, W.-T. 2005. Biofilm formation characteristics of bacterial  
 1183 isolates retrieved from a reverse osmosis membrane. *Environmental Science &*  
 1184 *Technology*, 39, 7541-7550.
- 1185 Peretz, S. & Regev, O. 2012. Carbon nanotubes as nanocarriers in medicine. *Current Opinion in*  
 1186 *Colloid & Interface Science*, 17, 360-368.
- 1187 Petersen, E. J. & Henry, T. B. 2012. Methodological considerations for testing the ecotoxicity of  
 1188 carbon nanotubes and fullerenes: Review. *Environmental Toxicology and Chemistry*, 31,  
 1189 60-72.
- 1190 Petersen, E. J., Zhang, L., Mattison, N. T., O'carroll, D. M., Whelton, A. J., Uddin, N., Nguyen, T.,  
 1191 Huang, Q., Henry, T. B., Holbrook, R. D. & Chen, K. L. 2011. Potential Release Pathways,  
 1192 Environmental Fate, And Ecological Risks of Carbon Nanotubes. *Environmental Science &*  
 1193 *Technology*, 45, 9837-9856.
- 1194 Plata, D. L., Reddy, C. M. & Gschwend, P. M. 2012. Thermogravimetry–Mass Spectrometry for  
 1195 Carbon Nanotube Detection in Complex Mixtures. *Environmental Science & Technology*,  
 1196 46, 12254-12261.
- 1197 Qu, X., Alvarez, P. J. J. & Li, Q. 2012. Impact of Sunlight and Humic Acid on the Deposition Kinetics  
 1198 of Aqueous Fullerene Nanoparticles (nC60). *Environmental Science & Technology*, 46,  
 1199 13455-13462.
- 1200 Reid, B. J., Stokes, J. D., Jones, K. C. & Semple, K. T. 2000. Nonexhaustive Cyclodextrin-Based  
 1201 Extraction Technique for the Evaluation of PAH Bioavailability. *Environmental Science &*  
 1202 *Technology*, 34, 3174-3179.

1203 Ren, X., Chen, C., Nagatsu, M. & Wang, X. 2011. Carbon nanotubes as adsorbents in  
1204 environmental pollution management: A review. *Chemical Engineering Journal*, 170, 395-  
1205 410.

1206 Rhodes, A. H., Carlin, A. & Semple, K. T. 2008a. Impact of Black Carbon in the Extraction and  
1207 Mineralization of Phenanthrene in Soil. *Environmental Science & Technology*, 42, 740-745.

1208 Rhodes, A. H., Dew, N. M. & Semple, K. T. 2008b. Relationship between cyclodextrin extraction  
1209 and biodegradation of phenanthrene in soil. *Environmental Toxicology and Chemistry*, 27,  
1210 1488-1495.

1211 Rhodes, A. H., Riding, M. J., Mcallister, L. E., Lee, K. & Semple, K. T. 2012. Influence of Activated  
1212 Charcoal on Desorption Kinetics and Biodegradation of Phenanthrene in Soil.  
1213 *Environmental Science & Technology*, 46, 12445-12451.

1214 Richards, J. J., Rice, A. H., Nelson, R. D., Kim, F. S., Jenekhe, S. A., Luscombe, C. K. & Pozzo, D. C.  
1215 2012. Modification of PCBM Crystallization Via Incorporation of C60 in Polymer/Fullerene  
1216 Solar Cells. *Advanced Functional Materials*, 23, 514-522.

1217 Riding, M. J., Martin, F. L., Trevisan, J., Llabjani, V., Patel, I., Jones, K. C. & Semple, K. T. 2012a.  
1218 Concentration-dependent effects of carbon nanoparticles in gram-negative bacteria  
1219 determined by infrared spectroscopy with multivariate analysis. *Environmental Pollution*,  
1220 163, 226-234.

1221 Riding, M. J., Trevisan, J., Hirschmugl, C. J., Jones, K. C., Semple, K. T. & Martin, F. L. 2012b.  
1222 Mechanistic insights into nanotoxicity determined by synchrotron radiation-based  
1223 Fourier-transform infrared imaging and multivariate analysis. *Environment International*,  
1224 50, 56-65.

1225 Roy, S. B. & Dzombak, D. A. 1998. Sorption nonequilibrium effects on colloid-enhanced transport  
1226 of hydrophobic organic compounds in porous media. *Journal of Contaminant Hydrology*,  
1227 30, 179-200.

1228 Sanchez, P. A. 1976. *Properties and management of soils in the tropics*, New York, USA, John Wiley  
1229 and Sons.

1230 Sayes, C. M., Fortner, J. D., Guo, W., Lyon, D., Boyd, A. M., Ausman, K. D., Tao, Y. J., Sitharaman,  
1231 B., Wilson, L. J., Hughes, J. B., West, J. L. & Colvin, V. L. 2004. The Differential Cytotoxicity  
1232 of Water-Soluble Fullerenes. *Nano Letters*, 4, 1881-1887.

1233 Schierz, A., Parks, A. N., Washburn, K. M., Chandler, G. T. & Ferguson, P. L. 2012. Characterization  
1234 and Quantitative Analysis of Single-Walled Carbon Nanotubes in the Aquatic Environment  
1235 Using Near-Infrared Fluorescence Spectroscopy. *Environmental Science & Technology*, 46,  
1236 12262-12271.

1237 Schreiner, K. M., Filley, T. R., Blanchette, R. A., Bowen, B. B., Bolskar, R. D., Hockaday, W. C.,  
1238 Masiello, C. A. & Raebiger, J. W. 2009. White-Rot Basidiomycete-Mediated Decomposition  
1239 of C60 Fullerol. *Environmental Science & Technology*, 43, 3162-3168.

1240 Semple, K. T., Doick, K. J., Jones, K. C., Burauel, P., Craven, A. & Harms, H. 2004. Peer Reviewed:  
1241 Defining Bioavailability and Bioaccessibility of Contaminated Soil and Sediment is  
1242 Complicated. *Environmental Science & Technology*, 38, 228A-231A.

1243 Semple, K. T., Riding, M. J., Mcallister, L. E., Sopena-Vazquez, F. & Bending, G. D. 2013. Impact of  
1244 black carbon on the bioaccessibility of organic contaminants in soil. *Journal of Hazardous  
1245 Materials*, 261, 808-816.

1246 Sen, T. K. & Khilar, K. C. 2006. Review on subsurface colloids and colloid-associated contaminant  
1247 transport in saturated porous media. *Advances in Colloid and Interface Science*, 119, 71-  
1248 96.

1249 Shan, J., Jiang, B., Yu, B., Li, C., Sun, Y., Guo, H., Wu, J., Klumpp, E., Schäffer, A. & Ji, R. 2011.  
1250 Isomer-Specific Degradation of Branched and Linear 4-Nonylphenol Isomers in an Oxidic  
1251 Soil. *Environmental Science & Technology*, 45, 8283-8289.

1252 Sharma, P. & Ahuja, P. 2008. Recent advances in carbon nanotube-based electronics. *Materials  
1253 Research Bulletin*, 43, 2517-2526.

- 1254 Shaw, G. & Connell, D. 1994. Prediction and Monitoring of the Carcinogenicity of Polycyclic  
1255 Aromatic Compounds (PACs). In: Ware, G. (ed.) *Reviews of Environmental Contamination  
1256 and Toxicology*. Springer New York.
- 1257 Shieh, Y.-T., Liu, G.-L., Wu, H.-H. & Lee, C.-C. 2007. Effects of polarity and pH on the solubility of  
1258 acid-treated carbon nanotubes in different media. *Carbon*, 45, 1880-1890.
- 1259 Simon-Deckers, A. L., Loo, S., Mayne-L'hermite, M., Herlin-Boime, N., Menguy, N., Reynaud, C. C.,  
1260 Gouget, B. & Carrière, M. 2009. Size-, Composition- and Shape-Dependent Toxicological  
1261 Impact of Metal Oxide Nanoparticles and Carbon Nanotubes toward Bacteria.  
1262 *Environmental Science & Technology*, 43, 8423-8429.
- 1263 Singh, P. & Cameotra, S. S. 2004. Enhancement of metal bioremediation by use of microbial  
1264 surfactants. *Biochemical and Biophysical Research Communications*, 319, 291-297.
- 1265 Singh, R., Paul, D. & Jain, R. K. 2006. Biofilms: implications in bioremediation. *Trends in  
1266 Microbiology*, 14, 389-397.
- 1267 Smith, B., Wepasnick, K., Schrote, K. E., Bertele, A. R., Ball, W. P., O'melia, C. & Fairbrother, D. H.  
1268 2008. Colloidal Properties of Aqueous Suspensions of Acid-Treated, Multi-Walled Carbon  
1269 Nanotubes. *Environmental Science & Technology*, 43, 819-825.
- 1270 Smith, B., Wepasnick, K., Schrote, K. E., Cho, H.-H., Ball, W. P. & Fairbrother, D. H. 2009. Influence  
1271 of Surface Oxides on the Colloidal Stability of Multi-Walled Carbon Nanotubes: A  
1272 Structure–Property Relationship. *Langmuir*, 25, 9767-9776.
- 1273 Snow, E. S., Perkins, F. K., Houser, E. J., Badescu, S. C. & Reinecke, T. L. 2005. Chemical Detection  
1274 with a Single-Walled Carbon Nanotube Capacitor. *Science*, 307, 1942-1945.
- 1275 Sobek, A. & Bucheli, T. D. 2009. Testing the resistance of single- and multi-walled carbon  
1276 nanotubes to chemothermal oxidation used to isolate soots from environmental samples.  
1277 *Environmental Pollution*, 157, 1065-1071.
- 1278 Sollins, P., Robertson, G. P. & Uehara, G. 1988. Nutrient mobility in variable- and permanent-  
1279 charge soils. *Biogeochemistry*, 6, 181-199.
- 1280 Stokes, J. D., Paton, G. I. & Semple, K. T. 2005. Behaviour and assessment of bioavailability of  
1281 organic contaminants in soil: relevance for risk assessment and remediation. *Soil Use and  
1282 Management*, 21, 475-486.
- 1283 Terashima, M. & Nagao, S. 2007. Solubilization of [60]Fullerene in water by aquatic humic  
1284 substances. *Chemistry Letters*, 36, 302-303.
- 1285 Tong, Z., Bischoff, M., Nies, L., Applegate, B. & Turco, R. F. 2007. Impact of Fullerene (C60) on a  
1286 Soil Microbial Community. *Environmental Science & Technology*, 41, 2985-2991.
- 1287 Towell, M. G., Browne, L. A., Paton, G. I. & Semple, K. T. 2011. Impact of carbon nanomaterials on  
1288 the behaviour of 14C-phenanthrene and 14C-benzo-[a] pyrene in soil. *Environmental  
1289 Pollution*, 159, 706-715.
- 1290 Turco, R. F., Bischoff, M., Tong, Z. H. & Nies, L. 2011. Environmental implications of nanomaterials:  
1291 are we studying the right thing? *Current Opinion in Biotechnology*, 22, 527-532.
- 1292 Upadhyayula, V. K. K., Deng, S., Smith, G. B. & Mitchell, M. C. 2009. Adsorption of *Bacillus subtilis*  
1293 on single-walled carbon nanotube aggregates, activated carbon and NanoCeram™. *Water  
1294 Research*, 43, 148-156.
- 1295 Upadhyayula, V. K. K. & Gadhamshetty, V. 2010. Appreciating the role of carbon nanotube  
1296 composites in preventing biofouling and promoting biofilms on material surfaces in  
1297 environmental engineering: A review. *Biotechnology Advances*, 28, 802-816.
- 1298 Velasco-Santos, C., Martinez-Hernandez, A. L., Consultchi, A., Rodriguez, R. & Castaño, V. M. 2003.  
1299 Naturally produced carbon nanotubes. *Chemical Physics Letters*, 373, 272-276.
- 1300 Wang, L., Fortner, J. D., Hou, L., Zhang, C., Kan, A. T., Tomson, M. B. & Chen, W. 2012a.  
1301 Contaminant-mobilizing capability of fullerene nanoparticles (nC60): Effect of solvent-  
1302 exchange process in nC60 formation. *Environmental Toxicology and Chemistry*, 32, 329-  
1303 336.
- 1304 Wang, L., Huang, Y., Kan, A. T., Tomson, M. B. & Chen, W. 2012b. Enhanced Transport of 2,2',5,5'-  
1305 Polychlorinated Biphenyl by Natural Organic Matter (NOM) and Surfactant-Modified  
1306 Fullerene Nanoparticles (nC60). *Environmental Science & Technology*, 46, 5422-5429.

1307 Wang, P. & Keller, A. A. 2009. Natural and Engineered Nano and Colloidal Transport: Role of Zeta  
1308 Potential in Prediction of Particle Deposition. *Langmuir*, 25, 6856-6862.

1309 Wang, P., Shi, Q., Liang, H., Steuerman, D. W., Stucky, G. D. & Keller, A. A. 2008a. Enhanced  
1310 Environmental Mobility of Carbon Nanotubes in the Presence of Humic Acid and Their  
1311 Removal from Aqueous Solution. *Small*, 4, 2166-2170.

1312 Wang, X., Lu, J. & Xing, B. 2008b. Sorption of Organic Contaminants by Carbon Nanotubes:  
1313 Influence of Adsorbed Organic Matter. *Environmental Science & Technology*, 42, 3207-  
1314 3212.

1315 Wang, X., Shu, L., Wang, Y., Xu, B., Bai, Y., Tao, S. & Xing, B. 2011. Sorption of Peat Humic Acids to  
1316 Multi-Walled Carbon Nanotubes. *Environmental Science & Technology*, 45, 9276-9283.

1317 Wang, X., Tao, S. & Xing, B. 2009. Sorption and Competition of Aromatic Compounds and Humic  
1318 Acid on Multiwalled Carbon Nanotubes. *Environmental Science & Technology*, 43, 6214-  
1319 6219.

1320 Xia, X., Li, Y., Zhou, Z. & Feng, C. 2010. Bioavailability of adsorbed phenanthrene by black carbon  
1321 and multi-walled carbon nanotubes to Agrobacterium. *Chemosphere*, 78, 1329-1336.

1322 Xia, X., Zhou, C., Huang, J., Wang, R. & Xia, N. 2013. Mineralization of phenanthrene sorbed on  
1323 multiwalled carbon nanotubes. *Environmental Toxicology and Chemistry*, 32, 894-901.

1324 Yan, H., Pan, G., Zou, H., Li, X. & Chen, H. 2004. Effective removal of microcystins using carbon  
1325 nanotubes embedded with bacteria. *Chinese Science Bulletin*, 49, 1694-1698.

1326 Yang, K., Wang, X., Zhu, L. & Xing, B. 2006a. Competitive Sorption of Pyrene, Phenanthrene, and  
1327 Naphthalene on Multiwalled Carbon Nanotubes. *Environmental Science & Technology*, 40,  
1328 5804-5810.

1329 Yang, K. & Xing, B. 2007. Desorption of polycyclic aromatic hydrocarbons from carbon  
1330 nanomaterials in water. *Environmental Pollution*, 145, 529-537.

1331 Yang, K., Zhu, L. & Xing, B. 2006b. Adsorption of Polycyclic Aromatic Hydrocarbons by Carbon  
1332 Nanomaterials. *Environmental Science & Technology*, 40, 1855-1861.

1333 Zhang, L., Hou, L., Wang, L., Kan, A. T., Chen, W. & Tomson, M. B. 2012a. Transport of Fullerene  
1334 Nanoparticles (nC60) in Saturated Sand and Sandy Soil: Controlling Factors and Modeling.  
1335 *Environmental Science & Technology*, 46, 7230-7238.

1336 Zhang, L., Petersen, E. J. & Huang, Q. 2011a. Phase Distribution of 14C-Labeled Multiwalled  
1337 Carbon Nanotubes in Aqueous Systems Containing Model Solids: Peat. *Environmental  
1338 Science & Technology*, 45, 1356-1362.

1339 Zhang, L., Petersen, E. J., Zhang, W., Chen, Y., Cabrera, M. & Huang, Q. 2012b. Interactions of 14C-  
1340 labeled multi-walled carbon nanotubes with soil minerals in water. *Environmental  
1341 Pollution*, 166, 75-81.

1342 Zhang, L., Wang, L., Zhang, P., Kan, A. T., Chen, W. & Tomson, M. B. 2011b. Facilitated Transport  
1343 of 2,2',5,5'-Polychlorinated Biphenyl and Phenanthrene by Fullerene Nanoparticles  
1344 through Sandy Soil Columns. *Environmental Science & Technology*, 45, 1341-1348.

1345 Zhang, S., Shao, T. & Karanfil, T. 2011c. The effects of dissolved natural organic matter on the  
1346 adsorption of synthetic organic chemicals by activated carbons and carbon nanotubes.  
1347 *Water Research*, 45, 1378-1386.

1348 Zhou, W., Shan, J., Jiang, B., Wang, L., Feng, J., Guo, H. & Ji, R. 2013. Inhibitory effects of carbon  
1349 nanotubes on the degradation of 14C-2,4-dichlorophenol in soil. *Chemosphere*, 90, 527-  
1350 534.

1351

1352

1353