

Carbon nanomaterials in clean and contaminated soils: environmental implications and applications

Matthew J. Riding, Francis L. Martin, Kevin C. Jones, Kirk T. Semple

Response to referee comments

We thank the two referees for their comments and well thought through constructive criticism. We have endeavoured to address each point individually, and have either modified the script accordingly or provided additional justification for an alternative response.

If you require additional information or clarification of points, we will be happy to elaborate further.

Referee #1

The paper explored implication and application of carbon nanomaterials (CNMs) in clean and contaminated soils. CNMs can interact with hydrophobic organic contaminants (HOCs), and thus have an impact on the persistence, mobility and bioavailability of contaminants within soils. Overall, this review paper is well written, and the whole paper flows smoothly. It is one of the excellent papers I have read on an open-access journal. There are only several minor things that need to be addressed. Specific comments, following the order of the manuscript, are listed below.

- 1) Authors have discussed many aspect of CNM in soils. One question would be: what will be the realistic concentration of anthropogenic CNM in the soil?

As CNMs are an emerging material, predicting a “realistic [future] concentration of anthropogenic CNMs in the soil” is exceptionally difficult. Not only are new applications for CNMs being regularly found, legislation regarding their production, use and disposal is still a rapidly evolving area of study. There are some papers which have attempted to estimate the future CNM concentration in soils, and these are all evaluated in an excellent review (Holden et al. 2014, *ES&T in press* DOI: 10.1021/es502440s), which has been added as a citation in the paper.

- 2) If their concentration is extremely small, what will be the critical concentration level that can exhibit toxicity?

This is a good question, and can be addressed with reference to the review article cited in the comment above. The critical concentration at which CNMs will exhibit toxicity is extremely difficult to measure/predict for a number of reasons: (i) variations in target organism (discussed in the script in Section 5.1); (ii) variations in soil type (discussed pp. 175 L27); (iii) variations in particle characteristics (discussed throughout the script); (iv) uncertainty calculating the organism’s exposure level from a particular concentration in the environment. To my knowledge, there are no papers that have consistently demonstrated toxicity results based on standard measures of toxicity (such as NOEL or LD50) for CNMs between soil/CNM types or target organisms. Based on the current level of understanding portrayed in the literature, we feel it is not possible to either categorically state or predict the level at which toxicity will occur, nor is it possible to predict whether any potentially

observed impacts will be caused by a direct result of CNMs (e.g. membrane damage by reactive oxygen species) or indirect result (sorption and reduced bioavailability/accessibility of food source). We feel that these barriers to estimating the toxicity of CNMs in the environment are sufficiently dealt with throughout the script.

- 3) If there is another scenario that we have to apply CNM to the soil, what is the potential application of CNM to soil?

This question lacks clarity and I am unable to understand the point it is attempting to raise. The paper concludes on pp.186 L3 that the future application of CNMs to soil should be assessed on a case-by-case basis.

- 4) Page 153, likely the section of “Carbon nanomaterial diversity and detection” focuses more on the diversity of CNMs, however, not on detection. If authors can summarize a table about the detection methods of CNMs in soil or other complicated matrix, it will be very helpful for readers who are interested in this topic. I have listed a few papers talking about the detection of CNMs:

(a), Detection of carbon nanotubes in environmental matrices using programmed thermal analysis K Doudrick, P Herckes, P Westerhoff - Environmental science & technology, 2012

(b) Thermogravimetry–Mass Spectrometry for Carbon Nanotube Detection in Complex Mixtures, Desirée L. Plata, Christopher M. Reddy, and Philip M. Gschwend, Environmental science & technology, 2012

(c) Characterization and Quantitative Analysis of Single-Walled Carbon Nanotubes in the Aquatic Environment Using Near-Infrared Fluorescence Spectroscopy, Ariette Schierz, Ashley N. Parks, Kathryn M. Washburn, G. Thomas Chandler, and P. Lee Ferguson, Environmental science & technology, 2012

We thank the referee for noticing this. The paper was deficient in its discussion of CNM detection methods within environmental matrices. We have fully complied with the referee’s suggestion.

- 5) Page 160, line 28, authors have mentioned about “the physicochemical properties of pristine nC60” depends on the “method of synthesis and preparation”. Please clarify how could the synthesis and preparation affect the property of nC60. Additionally, would the preparation method of nC60 affect the toxicity behaviour in soils?

We have removed the word synthesis. The impact of preparation methods is discussed at length in the sentences and paragraphs that immediately follow the sentence in question. For example, we discuss the influence of sonication and suspension media, both of which are particle preparation methods. We do not think it is possible to provide any additional information to that which is already presented.

Referee #2

This review is relevant as it joins information about the fate and behaviour of one main types of nanomaterials, that is being produced and applied in large quantities. However, the paper needs some structural reformulations that are highlighted in comments made in the PDF of the manuscript. Hence, I think that it could be accepted after major revisions.

The role of some soil properties in CNMs fate and behaviour was forgotten, for example, the role of clay particles.

We have added additional information to the script, specifically related to clay particles.

The toxicity section is very poor developed and only toxicity to soil microbial community was mentioned. Invertebrates and plants were not mentioned. If no information exists for this group of organisms, (but I know that some is available), at least this needs to be mentioned.

One of the key aims of the aim of the paper is to specifically discuss the implications of CNMs on terrestrial microbiota, and the possible impact on contaminant bio-degradation. This is discussed at considerable length (13 pages) in Section 5. It was never the intention of the script to consider macro flora or fauna. The scope of the script is clearly stated in the final paragraph of Section 1. We do not feel that toxicity information for additional organisms should be added.

[The toxicity] section should appear after the description of the effects of the biological activity on CNMs in soils.

The section has been moved as suggested.

It remained unclear, if these CNMs can be degraded or not by soil microorganisms. Or at least the role of soil microorganisms in functional groups and in the subsequent stability of these CNMs. If this information does not exist, this should be mentioned in the manuscript.

We agree that the section lacked clarity and we have modified the text accordingly.

It would also be mentioned, or at least reinforced that studies available aimed to perceive the role of physical and chemical properties on the fate of CNMs in the soil, but any attempt was made to perceive how soil physical and chemical properties together with the biological activity determine the modification of such CNMs and its fate. This has to be made in more real environmental scenarios, and at least the authors should call the attention for this necessity.

This is an excellent point, which to some extent is already mentioned in the first paragraph of the conclusion. We have updated this section to include the additional information that the referee recommends.

Further through all the manuscript the most relevant results of several studies are described without any criticisms, and some important aspects of the experimental design of the studies were not added. I have exemplified this also in some comments.

We have amended the script to address the comments provided in the annotated PDF.

The pathways for the entrance of CNMs in the soils need to be clearly mentioned in the manuscript.

Addressed by adding citation to:

Köhler, A. R., Som, C., Helland, A. & Gottschalk, F. 2008. Studying the potential release of carbon nanotubes throughout the application life cycle. *Journal of Cleaner Production*, 16, 927-937.

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 of sorbed contaminants and the toxicity of CNMs is required before their sorptive abilities
17 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 C₆₀ 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 sp² 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 C₆₀ 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). C₆₀ 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-C₆₀ (nC₆₀) particles (regarded as the most environmentally relevant
81 form), which are crystalline structures containing 100-1000 C₆₀ 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 organic chemicals with well-defined structures, the diversity of particle sizes, lengths,
85 diameters, charges, surface areas, coatings, molecular weight, impurities and aggregation states,
86 which are often specific to their particular environmental compartment and not necessarily
87 constant, limits their detection and characterisation in soils [and other complex environmental](#)
88 [matrices](#) through chromatographic techniques (Petersen et al., 2011). A summary of methods
89 used to detect CNMs within soils and sediments is presented in Table 1.

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

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

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91 In addition, as the life cycles of CNM containing products are likely to vary greatly, the
92 ~~routes~~means by which these materials enter the soil environment ~~is~~are also likely to be highly
93 variable (Pan and Xing, 2012). An excellent review of different CNM exposure scenarios for both
94 humans and the environment, is provided by Köhler et al. (2008). Further complicating their
95 detection is the emerging nature of manufactured CNMs as soil xenobiotic components, and
96 hence their presently low concentrations, together with their interaction with naturally occurring
97 nanomaterials and other environmental components, which leads to particles with sizes and
98 compositions that significantly differ from their native forms (Nowack and Bucheli, 2007;
99 Darlington et al., 2009; Chen et al., 2011). As such, careful consideration of multiple
100 environmental variables is required 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~~OM~~ plays a substantial role in both the fate and behaviour of CNMs
114 through alterations in the dominance of the various DLVO and non-DLVO interactions. SOM
115 (which 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 π - π or CH- π 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^{2+} 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
148 a 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, however, may behave
158 have a different impact differently to that of molecular DOM under environmentally relevant ionic
159 conditions. This could be caused by the alteration of as-particle phase distributions may be
160 altered due to the direct sorption of CNMs, as well as the possibility of DOM or cations being
161 release from the soil particles themselves (Zhang et al., 2011a). In the absence of sodium ions,
162 Zhang et al. (2011a) found no adsorption of MWCNTs to solid peat, indicating a limited affinity of
163 DOM-MWCNT composites towards the solid phase relative to the aqueous phase, possibly due to
164 electrostatic repulsion and hydrophilicity of DOM coated nanotubes. With the addition of Na^+
165 ions, the relative affinity between DOM-MWCNTs and peat was increased due to reductions in the
166 charge potential and subsequent increase in interactions occurring through hydrophobic
167 interactions and/or vdW attraction (Zhang et al., 2011a). Zhang et al. (2011a) concluded that with

168 | increasing ionic strength ~~γ~~ (such as in environments containing seawater or hard freshwater), ~~γ~~, an
169 | increased precipitation of MWCNTs from the aqueous phase will occur, impeding their transport
170 | within the environment.

171 | Consideration of the ζ -potential (diffuse surface charge) of CNMs in relation to the soil matrix
172 | is important when considering the dynamics of smaller particles dispersal, transport and
173 | deposition, for which charge forces are likely to be highly influential relative to larger particles or
174 | agglomerates (Darlington et al., 2009). Its measure, in part, provides information on the likely
175 | mobility, rates of interaction and aggregation status due to electrostatic forces generated by
176 | charged surfaces (Hu et al., 2005; Jafar and Hamzeh, 2013). Pristine CNTs typically express limited
177 | surface charge (Mohanty et al., 2007); however, Wang et al. (2008a) found that the ζ -potential of
178 | CNTs with a HA coating was highly negative, which resulted in electrostatic repulsion between the
179 | particles and hence stability when partitioned into the aqueous phase. They concluded that
180 | mobility and environmental transport within typically negatively charged porous media, such as
181 | certain types of soils was highly likely, with particles remaining stable over a wide range of ionic
182 | strengths (Wang et al., 2008a). A reduction in pH to the point at which the CNTs had no charge
183 | was identified as an effective means of causing CNTs to precipitate, through the destabilization of
184 | the HA coatings (Wang et al., 2008a).

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

193 containing carbohydrates and predominantly hydrophilic domains resulted in limited dispersal
194 (Chappell et al., 2009).

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

201 *3.2 The impact of soil inorganic matter*

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

219 [surfactants from solution by clay minerals and \(ii\) clay minerals bridging between MWCNTs and](#)
220 [surfactants \(Han et al., 2008\).](#)

221 [Furthermore, the charge characteristics of soils can also influence the behaviour and fate of](#)

222 [CNMs](#). Broadly, all soils can be divided into two groups; permanent-charge (P-C) and variable-
223 charge (V-C) (Sollins et al., 1988). In P-C soils, the substitution of ions with lower valence for ions
224 with higher valence results in the alteration of crystal lattice structures within layer-silicate clays
225 (illite, smectite, chlorite and kaolin), and a permanent charge deficit, which persists irrespective of
226 variations in the composition of soil solutions and pH (Sollins et al., 1988). In V-C soils, protonation
227 and de-protonation of surface hydroxyl groups results in the positive charge and hence anion
228 exchange capacity (AEC); whereas deprotonation results in cation exchange capacity (CEC) (Sollins
229 et al., 1988). The structure of V-C soils is also modified in response to increasing pH, resulting in
230 increased repulsion and more limited aggregation (Sollins et al., 1988). Both P-C and V-C surfaces
231 are present in all soil types; however, only one charge system typically dominates, dictated largely
232 by soil mineralogy (Sollins et al., 1988). While V-C soils occur more frequently in tropical regions
233 due to the typical mineralogical composition which forms under humid, warm conditions, they do
234 not occur ubiquitously, and many areas with predominantly P-C characteristics occur (Sanchez,
235 1976; Sollins et al., 1988). Hence, while V-C soils represent a small fraction of global soil types,
236 interactions between nanoparticles and soils are likely to be much more dynamic relative to those
237 with a P-C. Despite this, almost all investigations have predominantly focused on P-C soils,
238 restricting the applicability of CNM fate and behaviour investigations.

239 The behaviour of CNMs in V-C soils has been assessed by Zhang et al. (2012b), who
240 investigated the stability of MWCNTs suspended in water with soil minerals kaolinite, smectite
241 and shale over a range of sodium concentrations. Without additional Na^+ , no significant difference
242 in the stability of MWCNTs between each of the soil minerals was observed; however, with
243 increasing ionic strength, the removal of MWCNTs from the aqueous phase followed the order
244 smectite > kaolinite > shale (weakest to largest MWCNT association). As ionic strength increased,

245 the MWCNT removal tendency for smectite and kaolinite was inversely correlated to the mineral
246 surface potential. However, the electrostatic potential of shale is higher than either kaolinite or
247 smectite, yet shale demonstrated the strongest sorption of MWCNTs (Zhang et al., 2012b). This
248 was attributed to the large, hydrophobic, organic content of shale, which is able to strongly sorb
249 MWCNTs. Hence, under these soil conditions, the transport of CNMs in soils is directly correlated
250 with mineral hydrophobicity, but inversely correlated with surface potential (Zhang et al., 2012b).
251 It is therefore imperative that studies of nanomaterial fate and behaviour in soils include detailed
252 information regarding soil mineralogy.

253 *3.3 The impact of CNM preparation methods, functional groups and UV exposure*

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

270 Typically, agglomeration of CNMs in the presence of divalent (Ca^{2+}) cations occurs to a greater
271 extent than with monovalent (Na^+) cations. However, when exposed to solar irradiation, $n\text{C}_{60}$ can
272 undergo surface oxidation and decomposition (Hou and Jafvert, 2008; 2009), with large
273 implications for environmental behaviour and fate (Qu et al., 2012). Following exposure to UV-A
274 (the largest component of UV in sunlight), the oxygen containing functional groups formed on
275 $n\text{C}_{60}$ hindered aggregation in NaCl solutions due to their elevated hydrophilicity and negative
276 surface charge (Hou and Jafvert, 2009). Conversely, neutralisation of the negative surface charge
277 on oxidised $n\text{C}_{60}$ due to interactions with Ca^{2+} ions when suspended in CaCl_2 can result in particle
278 agglomeration (Li and Liang, 2007). This potentially occurs due to the charge screening ability of
279 Ca^{2+} relative to Na^+ , which reduces the stability of colloids (Li and Liang, 2007). Qu et al. (2012)
280 expanded upon this work through studying the effects of UV-A exposure for either 20 h or 7 d on
281 the rate of deposition and the attachment efficiency of $n\text{C}_{60}$ on to silica bead surfaces. The
282 stability of $n\text{C}_{60}$ increased proportionally with increasing UV-A exposure time against aggregation
283 in solutions containing NaCl, which was attributed to the increase in surface oxidation and
284 hydrophilicity (Qu et al., 2012). Further, while the attachment efficiency of $n\text{C}_{60}$ exposed to UV-A
285 for 7 d was at a maximum in NaCl concentrations of 250 mM, attachment decreased following an
286 increase in NaCl concentration to 300 mM. This indicates that stability of $n\text{C}_{60}$ containing oxygen
287 surface functional groups was attributed to the hydration force and not DLVO forces, which was
288 more significant with the 7 d UV exposed $n\text{C}_{60}$ than either the pristine or the 20 h UV due to the
289 greater hydrophilicity (Qu et al., 2012).

290 In other investigations, surface immobilisation of macromolecules, such as HAs at
291 environmentally relevant concentrations, has increased the solubility of C_{60} due to the effect of
292 steric hindrance caused by the sorbed SOM and a reduction in the hydrophobicity of the
293 nanoparticle surface, preventing re-aggregation and reducing attachment efficiency (Li et al.,
294 2009; Qu et al., 2012). However, Qu et al. (2012) found 7 d UV exposed $n\text{C}_{60}$ had negligible surface
295 sorption of either HWM or LMW HAs due to the negative surface charge and elevated surface

296 hydrophilicity. Hence, DOM is likely to be less significant in determining the suspension stability of
297 irradiated nC_{60} (Qu et al., 2012). A similar relationship may occur due to the formation of oxygen
298 containing hydroxyl- and carboxyl-groups on MWCNTs due to surface oxidation, which can
299 promote colloidal stability and hydrophilicity of CNTs in addition to inducing alterations to surface
300 charge (Shieh et al., 2007; Smith et al., 2009). This is illustrated by Hu et al. (2005), in which
301 carboxylic acid groups as a result of nitric acid treatment of SWCNTs had high ζ -potentials (-28
302 mV) over a pH range of 2-10, indicating their moderate stability in water in contrast to pristine
303 CNTs (Hu et al., 2005). Reduced deposition of pristine nC_{60} occurred on silica glass beads coated in
304 HMW HA than LMW HA due to steric hindrance (Qu et al., 2012). The effect was more
305 pronounced at lower ionic strengths due to electrostatic repulsion between charge groups
306 resulting in a more stretched-out conformation of HA molecules (Qu et al., 2012). However, both
307 HMW and LMW HA coated beads facilitated the deposition of 7 d UV exposed nC_{60} , with reduced
308 sensitivity to changes in ionic strength as a result of reduced steric hindrance (due to the compact
309 conformation of HAs at high ionic strengths (~ 60 mM)), lower surface potential and increased
310 hydrogen bonding between the oxygen containing groups of the functionalised nC_{60} and nitrogen-
311 and oxygen-groups on the HA (Qu et al., 2012).

312 Comparatively determining the relative importance of CNM functionalization and ionic
313 strength on CNTs and nC_{60} behaviour in soils is difficult due to the myriad of different
314 experimental configurations. To overcome this, Jaisi and Elimelech (2009) used carboxyl-
315 functionalised SWCNTs and nC_{60} (radius of 51 nm) in natural soil columns containing 29% clay and
316 pore sizes of 22 μm , to determine the impact of ionic strength on particle transport and
317 deposition. As ionic strength increased (0.03 – 100 mM), the rate of SWCNT deposition within the
318 soil column also increased, with the observed effect more apparent with divalent cations (Ca^{2+})
319 than monovalent cations (K^+). Interestingly, while nC_{60} was highly sensitive to variations in ionic
320 strength, far lower deposition rates were observed. It was proposed that the structure and shape
321 of SWCNTs, in particular their large aspect ratio and bulky agglomerated states, in addition to soil

322 particle heterogeneity increased the straining effect and retention by the soil matrix (Jaisi and
323 Elimelech, 2009). Nanomaterial structural conformation is therefore a further consideration in the
324 relative extent to which CNMs will be dispersed and transported within the soil, with nC_{60} more
325 likely to experience leaching than SWCNTs under a variety of solution chemistries (Jaisi and
326 Elimelech, 2009) within negatively charged soil media.

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

332

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

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

346 1) Sufficiently high concentration of nanoparticles

- 347 2) Mobility of the nanoparticles carrying sorbed HOCs
- 348 3) Sorbate toxicity even when present in trace quantities
- 349 4) The ratio of sorption to desorption relative to the timescale of particle mobility

350 The sorption affinity of CNMs for common environmental contaminants such as PAHs, known
351 to pose significant risks to both the environment and human health due to their toxic properties
352 (Menzie et al., 1992; Shaw and Connell, 1994; Cebulska-Wasilewska et al., 2007), has been
353 reported as over three orders of magnitude greater than that of natural soil/sediments (Yang et
354 al., 2006b). The potential for these emerging materials to become widespread in the soil
355 environment, particularly those with a strongly hydrophobic nature and large reactive surface
356 area, such CNMs, raises questions and concerns about the environmental consequences of their
357 release (Pan and Xing, 2010).

358 *4.1 CNM contaminant sorption and desorption in soils*

359 Understanding the adsorption and desorption of HOCs to CNMs in soils is critical to the
360 environmental risk assessment processes, as well as determining their potential applications as
361 environmental adsorbents (Yang et al., 2006a). As the fundamentals of CNM-HOC sorption have
362 been extensively reviewed, the reader is referred to a review by Ren et al. (2011) for a
363 comprehensive overview. This section addresses the manner in which soils may alter the HOC
364 sorption/desorption properties of CNMs, focusing specifically on two conflicting effects; (i) CNM
365 dispersal by DOM (increasing the surface area and hence the number of adsorption sites (Hyung
366 et al., 2006; Lin and Xing, 2008)); versus (ii) the formation of CNM-DOM coatings (blocking and/or
367 competing for adsorption sites reducing the number available for organic contaminants (Chen et
368 al., 2008; Wang and Keller, 2009; Cui et al., 2011; Wang et al., 2011; Zhang et al., 2011c)). The
369 relative importance of these two phenomena are poorly understood in relation to their sorption
370 and desorption of organic contaminants (Zhang et al., 2011c; Pan and Xing, 2012), and are highly
371 dependent on the nanoparticle properties, and the nature of SOM and the sorbate (Wang et al.,
372 2009; Zhang et al., 2011c; Lerman et al., 2013).

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

380 Wang et al. (2008b) assessed the extent to which HAs and peptone altered the sorption of
381 phenanthrene, naphthalene or 1-naphthol on-to MWCNTs (outer diameter of 40 nm), by fitting
382 sorption data with Freundlich and Polanyi models. Their results showed that each type of DOM
383 resulted in nonlinear sorption isotherms to the MWCNTs, following the order peptone > HAs.
384 Although the inherent sorptive ability of HA for each of the contaminants was more limited than
385 that of pristine MWCNTs, HA coatings did not result in large changes to the sorption of any of the
386 contaminants, which is inconsistent with models indicating that “fouling” of sorption sites by
387 DOM will reduce contaminant sorption capacity (Carter and Weber, 1994; Wang et al., 2008b).
388 The authors proposed that either uneven coating of the MWCNT by HA occurred, or that the
389 anticipated sorption reduction as a result of polar moieties from the HA coating, was offset due to
390 the increase in O-containing moieties resulting in particle repulsion and dispersal, exposing new
391 sites available for HOC sorption. Contrastingly, peptone, due to the large quantity sorbed relative
392 to each of the other DOM fractions, resulted in the largest reduction in available sorption sites
393 (Wang et al., 2008b). Similar interactions as to the relative ability of different OM coatings to alter
394 CNM sorption have been identified by Cui et al. (2011) and Gai et al. (2011). Although direct
395 comparison of the studies is not possible due to the different particles used, Cui et al. (2011)
396 found HAs, TAs and peptone pre-interacted with SWCNTs resulting in the formation of polar
397 functional groups on the nanotube surface, reducing the area available for phenanthrene sorption
398 in the order of peptone > TAs > HAs. Similarly, Gai et al. (2011) identified a reduction in C₆₀

399 agglomerate sizes due to the dispersal effects of HA, increasing atrazine sorption due to dispersal
400 and re-arrangement, rather than interactions between the atrazine and HA (Gai et al., 2011).
401 Hence, it may be argued that the impact of DOM on CNM-HOC sorption is dependent on the type
402 of OM present and possibly also CNM type.

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

424 mobilisation at 2 mg kg^{-1} , it was not possible to consider the desorption of contaminants if
425 transport were to occur.

426 An excellent study by Towell et al. (2011), assessed the extent to which HPCD extraction of
427 HOCs with different physicochemical properties desorbed from soils amended with CNMs at
428 concentrations between 0.05% and 0.5% (substantially larger than that employed by Li (2012)). At
429 concentrations $\geq 0.05\%$, Towell et al. (2011) identified significantly less $^{14}\text{C-B}[a]\text{P}$ extracted from
430 CNM amended soils than ^{14}C -phenanthrene due to the high hydrophobicity and $\log K_{ow}$ value
431 reducing the ability of $^{14}\text{C-B}[a]\text{P}$ to partition into the aqueous phase. This was exacerbated by the
432 relatively HMW of $^{14}\text{C-B}[a]\text{P}$, which has been proven as a critical factor determining the bonding
433 energy between SWCNTs and PAHs (Debnath et al., 2008; Towell et al., 2011). In relation to Factor
434 4, the nature of the sorbate may therefore influence the extent of desorption, and therefore the
435 duration for which contaminants will remain sorbed. It may be proposed that CNM sorbed HMW
436 HOCs represent a greater risk of increased distance of transportation within the environment than
437 LMW HOCs.

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

442 *4.2 CNM-HOC mobility*

443 Once sorbed to freely suspended CNMs within the soil matrix, the mobility of HOCs is
444 potentially increased; however, very few studies have focused on determining the impact of
445 CNMs on contaminant movement in soils. An overview of the basic principal of CNM facilitated
446 HOC transport is presented in Figure 1. Using column leach tests, Li (2012) examined the
447 behaviour of phenanthrene, fluorine, naphthalene and pyrene in a saturated sandy loam soil
448 amended with MWCNTs, functionalised MWCNTs (f-MWCNTs) and functionalised SWCNTs (f-

449 SWCNTs) at a concentration of 5 mg kg^{-1} . Significant retention of PAHs within the soil column was
450 observed, due to the strong sorption of contaminants by CNTs and their limited mobility within
451 the soil column (Li, 2012). In control soils and those amended with MWCNTs and f-MWCNTs,
452 retention of PAHs occurred in the order naphthalene < fluorine < phenanthrene < pyrene, with
453 hydrophobic interactions between the CNTs and PAHs cited as the predominant cause of the
454 observed pattern (Li, 2012). Contrastingly, retention of contaminants within soils amended with f-
455 SWCNTs occurred in the order of naphthalene > fluorine > phenanthrene > pyrene, the sorption of
456 which could not be accounted for by hydrophobic forces alone (Li, 2012). The trend was
457 negatively correlated to molecular size, indicating that larger sorbate molecules may have less
458 space for sorption due to the additional hydrophilic functional group (Yang et al., 2006b; Li, 2012).
459 It was concluded that leaching behaviours were determined by physical characteristics of both
460 CNTs and contaminants (Yang et al., 2006b; Li, 2012).

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

474 Zhang et al., 2011b; Wang et al., 2012a). CNMs may therefore be much more efficient at
475 enhancing the mobility of contaminants than natural colloidal materials.

476 Different processes of nC_{60} formation have also been identified as contributing to large
477 differences in their ability to alter the fate and transport of contaminants (Wang et al., 2012b).
478 Wang et al. (2012b) assessed nC_{60} samples prepared using either the standard solvent exchange
479 method, eight different types of SOM or surfactant modifications, or by the phase-transferring of
480 nC_{60} from a solution of toluene to either SOM or a surfactant (Wang et al., 2012b). Their results
481 indicated that while the mobility of nC_{60} was similar between each of the preparation methods,
482 the contaminant mobilising capability significantly differed. Relative to the unmodified nC_{60} ,
483 transport of PCBs through a saturated column of sandy soil increased by 42.2 – 227% with
484 surfactant modified nC_{60} , and by 233-370% with SOM-modified samples (Wang et al., 2012b). The
485 results were attributed to both increased adsorption affinities together with enhanced resistance
486 to desorption due to alterations to nC_{60} aggregation properties as a result of the SOM surfactant
487 (Wang et al., 2012b). During the process of aggregate formation, it is possible that a fraction of
488 SOM or another surfactant was intercalated within the C_{60} aggregates, significantly influencing the
489 porosity and geometry of the resulting nC_{60} aggregates, contributing to the enhanced desorption
490 resistance of PCBs (Wang et al., 2012b). With differing types of SOM and surfactants, variations in
491 the quantity and geometry of pores will occur, with the possibility that nC_{60} could be tailored to
492 specific physicochemical properties for use in *in situ* site remediation (Wang et al., 2012b). Hence,
493 the adsorption, desorption and transport of contaminants by nC_{60} will vary greatly depending on
494 the condition of its formation (Wang et al., 2012a).

495 Using a different approach, Hofmann and von der Kammer (2009) computer modelled the
496 extent to which CNMs could result in the movement of HOCs in soils under various scenario-based
497 conditions, to determine when relevant CNM transport of sorbed HOCs might occur. Worst-case
498 scenarios were adopted, assuming fully mobile CNMs within the porous medium, over a range of
499 realistic yet high CNM concentrations ($100 \text{ mg L}^{-1} - 1 \text{ g}^{-1}$) occurring in aggregate sizes of 10 – 100

500 mm. It was also assumed that CNMs were pre-equilibrated with the HOC at source and that
501 diffusion was the rate-limiting step for desorption (Hofmann and von der Kammer, 2009). From
502 this, it was possible to estimate the fraction of contaminants bound to CNMs at different
503 distances from the source over different time periods (days to years) using the Streamtube Model
504 for Advective and Reactive Transport (SMART) (Finkel et al., 1998), combined with the application
505 of retarded pore diffusion approximations (Bold et al., 2003) and combinations of two first-order
506 rate expressions (Cornelissen et al., 1997). The results showed that for aggregates of 100 nm, 2,
507 7, 40, 75, 82% of bound contaminants were transported > 1 m at nanoparticle concentrations of
508 0.1, 1, 10, 100, 1000 mg l⁻¹, respectively. Conversely, modelled transportation of contaminants
509 sorbed to aggregates of 10 nm in size were reduced to 0.1, 0.5, 3.6, 8% for the same respective
510 concentrations. Breakthrough of the 1 m modelled column did not occur in any of the considered
511 scenarios and all contaminants remained bound to the nanoparticle.

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

515 **Equation 1**

516 $Da_{NP} = \lambda s$

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

525 mobile CNM (Kretzschmar et al., 1999; Bold et al., 2003), resulting in limited nanoparticle
526 relocation of the contaminant (Hofmann and von der Kammer, 2009).

527 Hofmann and von der Kammer (2009) calculated Damköhler numbers for CNM aggregates of
528 different sizes and partitioning coefficients according to the rate constant data shown in Figure 2,
529 and based on different flow velocities of 1 m in 50 d (fast flow) – 1 m in 10 y (slow movement). It
530 was inferred that the CNM-contaminant transport mechanisms are strongly dependent on the
531 size of CNM agglomerates together with the distribution coefficients ($\log K_d$) (Hofmann and von
532 der Kammer, 2009). For example, Figure 2 shows contaminants sorbed to 1 mm aggregates at a
533 flow velocity of 1 m 50 d⁻¹ will not experience contaminant desorption until the $\log K_d$ of HOC-
534 CNMs is 8 m³ kg⁻¹, reaching equilibrium at $\log K_d$ 1 m³ kg⁻¹ (Hofmann and von der Kammer, 2009).
535 However, at a flow velocity of 1 m y⁻¹, decoupled transport will predominate for 1 mm aggregates
536 at a $\log K_d$ of 9 m³ kg⁻¹ reaching equilibrium at $\log K_d$ of 2 m³ kg⁻¹ (Hofmann and von der Kammer,
537 2009). It was concluded that under equilibrium sorption/desorption conditions, CNM mobility
538 resulted in negligible transport of sorbed contaminants (Hofmann and von der Kammer, 2009).
539 However, the mobility and concentration of CNMs becomes increasingly important in instances
540 with slow to very slow desorption (Hofmann and von der Kammer, 2009). While there are many
541 assumptions and simplifications associated with every modelling technique, the model identifies
542 scenarios in which transport and desorption of sorbed contaminant could potentially occur,
543 possibly providing useful guidelines for risk-assessment if applied on a case by case basis.
544 However, further work aimed specifically at validating the model against traditional column leach
545 tests in both V-C and P-C soils and additional desorption kinetics are urgent prerequisites.

546 From the above discussion, it can be concluded that each of the four factors identified by
547 Kretzschmar et al. (1999) for significant transport of contaminants by CNMs have been met.
548 However, more work examining the subsurface transport of CNMs through well-defined soils of
549 various types (such as clays, peats and silts) and CNMs with a variety of functional groups, sizes
550 and sorbed compounds in both saturated and unsaturated conditions are required (Jaisi and

551 Elimelech, 2009; Petersen et al., 2011). Of studies that are available, variation in experimental
552 conditions between the investigations renders comparisons of the efficiency of contaminant
553 mobility between CNM types tentative until standardised comparative testing is conducted.
554 Additionally, the molecular weights and sizes of CNMs may not be constant during their transport
555 within the soil environment, due to their physical, chemical or biological interaction with soil
556 components, which will likely influence their aggregation status, shape, surface charge (Pan and
557 Xing, 2012), and possibly also their ability to sorb and mobilise contaminants over long timescales.
558 Furthermore, definitive data of the desorption kinetics of HOCs from CNMs in soils are essential to
559 understanding their ability to transport contaminants (Ibaraki and Sudicky, 1995; Choi and Yavuz
560 Corapcioglu, 1997; Corapcioglu et al., 1999; Bold et al., 2003; Hofmann and von der Kammer,
561 2009), with slow desorption identified as a critical requirement (Roy and Dzombak, 1998). The
562 lack of experimentally derived desorption kinetic data from a range of soil types and conditions
563 makes determining the extent to which HOC sorption is strong enough, and desorption slow
564 enough, to allow CNMs to transport sorbed HOCs, and the associated implications of transport,
565 difficult to predict (Qu et al., 2012).

566

567 5. CNM – microorganism interactions

568 As soils represent one of the ultimate sinks for nanomaterials (Nowack and Bucheli, 2007),
569 terrestrial microorganisms, which interact directly with soils, may be significantly affected
570 (Navarro et al., 2008). [The reader is directed to an excellent review by Holden et al. \(2014\), which](#)
571 [evaluates the possible exposure concentrations of anthropogenic nanomaterials in a range of](#)
572 [environmental compartments, and assesses their relevance.](#) However, understanding the impact
573 of CNMs on the soil microbial community is a subject still in its infancy (Dinesh et al., 2012). If
574 CNMs within soils are bioaccessible to microflora, the possibility of disruption to bio-geochemical
575 processes within soils may be increased (Neal, 2008). This section discusses recent literature
576 related to [the modification of CNM fate and behaviour by microbiota, the](#) toxicity of CNMs in

577 | soils, ~~modification of CNM fate and behaviour by microbiota,~~ and the possible implications for
578 | the biodegradation of contaminants.

579 | ~~5.12~~ *Biological modification of CNMs in soils*

580 | The influence of microbial populations on the physical and chemical state of nanoparticles
581 | must ~~also~~ be considered when discussing the ultimate fate of nanomaterials (Aruguete and
582 | Hochella, 2010). Degradation of C₆₀ in aqueous solutions through photochemical processes have
583 | been identified by numerous investigations (Section 3.3) (Hou and Jafvert, 2008; Lee et al., 2009;
584 | Li et al., 2009), which may be an important step in both its breakdown and the activation of
585 | precursors for subsequent biological interactions (Turco et al., 2011). ~~A reduction in the size of~~
586 | ~~nC₆₀ aggregates and alterations to surface chemistry and solubility have been observed following~~
587 | ~~exposure to light (Hou and Jafvert, 2009; Lee et al., 2009). Lee et al. (2009) This suggests that~~
588 | ~~release of C₆₀ into soils could possibly result in the formation of photochemical products and~~
589 | ~~changes to C₆₀ molecular structure (Turco et al., 2011).~~ While C₆₀ photochemical reactions at the
590 | soil surface have not been studied, its oxidation and transformation to the more reactive fullerenol
591 | (i.e. C₆₀-OH) has been observed in water and in the presence of oxygen (Turco et al., 2011).
592 | Following the abiotic photochemical modification of C₆₀ through sunlight into fullerols (~~i.e. C₆₀-~~
593 | ~~OH~~), white-rot fungi was able to attack and subsequently incorporate a small amount of fullerol
594 | carbon into fungal biomass (lipids) after 32 weeks of decay (Schreiner et al., 2009). By contrast,
595 | unmodified C₆₀ was recalcitrant to such attack (Schreiner et al., 2009); hence, following minor
596 | surface alterations, biological interactions with C₆₀ were substantially altered, changing the fate of
597 | the particle. Similarly, the potential for horseradish peroxidase to biodegrade CNTs is strongly
598 | related to the presence of carboxyl groups on the nanotubes surface, which permitted enzyme
599 | mediated oxidation relative to pristine CNTs (Allen et al., 2008; Allen et al., 2009). Furthermore,
600 | Fenton's reagents oxidised carboxyl-functionalised SWCNTs (SWCNT-COOH) through the
601 | formation of hydroxyl radicals (Allen et al., 2008; Allen et al., 2009). It has therefore been

602 suggested that both white and brown rot mediated fungal activity could modify surface
603 functionalised CNTs in a similar manner to fullerenes (Turco et al., 2011).

604 Ultimately, Turco et al. (2011) suggested that the fate of C₆₀ in soil is potentially controlled by
605 the rate of abiotic alterations to the formation of more reactive precursors, as opposed to a
606 simple dose response, and the toxicity of UV-modified CNMs in soils has not yet been
607 investigated. If degradation of CNMs by fungi were to occur on a large scale in the natural
608 environment, their potential environmental risk would be significantly reduced; however, it is
609 unlikely to occur in sufficiently large quantities to efficiently reduce any possible burden of CNM
610 presence in soils.

611 | ~~5.24~~ CNM toxicity ~~to soil~~ microorganisms

612 The toxicity of CNMs is dependent upon the bioaccessibility of nanoparticles to bacteria, and
613 retention of some the nanoparticles reactivity (Neal, 2008). Currently, little literature is available
614 related to the toxicity of CNMs within soils (Dinesh et al., 2012). Hence, the discussion presented
615 here provides a theoretical estimation of the specific microbial communities that may be more
616 vulnerable to soil-borne CNMs, followed by an overview of recent CNM-amended soil toxicity
617 findings published within the literature.

618 Soil conditions will ultimately dictate the extent to which CNMs are able to interact with
619 terrestrial microflora. Based on the discussion earlier relating to the fate and behaviour of CNMs
620 in soils, in addition to information regarding cell properties (Mehmannavaz et al., 2001), it may be
621 possible to tentatively speculate as to the bioavailability or bioaccessibility of CNMs to different
622 microbial populations. When assessing nanotoxicity, consideration must be given to both the
623 likelihood of a nanoparticle coming into contact with microbial cells together with the initial
624 concentration added to soils, to provide an accurate means of estimating the particle availability
625 | (Dinesh et al., 2012). ~~It can be considered that a~~ strong interplay exists between the dispersal
626 status of nanoparticles and their bioaccessibility to specific soil microbial populations (Turco et al.,

627 2011). As bacteria frequently adhere to surfaces in the soil environment, attached cells within
628 biofilms constitute a large proportion of the bacterial community in the subsurface environment
629 (Neal, 2008). Neal (2008) therefore proposed that the study of nanotoxicity towards biofilm
630 communities is a more appropriate measure of toxicity in environmental systems than planktonic
631 cells. However, it is conceivable that given appropriate DLVO and non-DLVO forces between
632 CNMs, microorganisms and the soil matrix, CNMs could also become available to planktonic cells.
633 One example of which may be that CNM-SOM coatings could result in easier access to the cell
634 surface relative to uncoated particles due to the similarities in solubility between the cell
635 membrane and surfactant; however, the coating itself may attenuate the toxicity due to a lack of
636 physical contact between the CNM and a microbial cell (Lubick, 2008). Further work into the
637 conditions under which CNMs will be available to different microbial communities in soils is
638 needed.

639 The extent to which soils with different properties determine the toxicity of some CNMs was
640 directly investigated by Chung et al. (2011). The impact of MWCNTs at 50, 500 and 5000 μg^{-1} soil
641 on the activity of soil microorganisms in a sandy loam (pH 6.98, OC content 17.69 g kg^{-1} , CEC 13.51
642 ± 0.78) and loamy sand (pH 5.21, OC content 8.33 g kg^{-1} , CEC 9.05 ± 0.10) was considered. Based
643 on an analysis of the activity of enzymes involved with cycling carbon (1,4- β -glucosidase,
644 cellobiohydrolase, xylosidase), nitrogen (1,4- β -acetylglucosaminidase) and phosphatase together
645 with lower microbial biomass-nitrogen and carbon in soil, their results indicated that MWCNTs
646 exhibited antimicrobial properties within both soil types (Chung et al., 2011). As these findings are
647 consistent with culture studies outside of the soil environment, in which reduced microbial
648 activity was a result of membrane damage, physical piercing and oxidative stress (Kang et al.,
649 2007; Simon-Deckers et al., 2009), the authors assumed ~~similar that these~~ antimicrobial
650 mechanisms of action may be responsible. However, there is a strong argument against basing
651 assumptions of nanotoxicity mechanisms occurring in soils on those known to occur in culture
652 studies, due to typically large variations in test conditions.

653 Other investigations of nanotoxicity within soil using nC_{60} have found more limited toxicity
654 effects. For example, Johansen et al. (2008) found microbial respiration and biomass to be
655 unaffected by pristine C_{60} agglomerates (50 nm – 50 μm -size) applied at concentrations of 0, 5, 25
656 and 50 mg kg^{-1} to dry, clay loam textured soil containing 2.5% OM and with a pH of 6.7. However,
657 polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) measurements of
658 the diversity and number of bacteria over a 14 d period showed that a three to four fold reduction
659 in rapidly growing bacteria occurred immediately following the addition of C_{60} (Johansen et al.,
660 2008). The authors proposed the results may have been observed as a direct consequence of
661 reactive oxygen species (ROS) formed by the C_{60} , which disrupted DNA and lipids within
662 membranes (Johansen et al., 2008). However, confirmation of ROS damage could not be acquired
663 due to the complexity of the soil environment (Dinesh et al., 2012), and a recent publication by
664 Chae et al. (2012) casts some doubt on the extent to which ROS are generated in the presence of
665 SOM. It may therefore be considered more likely that the observed alterations to the diversity
666 and number of bacteria may be an indirect result of a reduction in nutrient bioavailability due to
667 adsorption by C_{60} (Johansen et al., 2008).

668 In a similar investigation, Tong et al. (2007) assessed the role aggregation status plays in
669 determining nanotoxicity within soils. The impact of either nC_{60} at 1 $\mu\text{g C}_{60} \text{g}^{-1}$ soil, or 1000 $\mu\text{g C}_{60} \text{g}^{-1}$
670 soil in granular form on the function and structure of soil microbial community was assessed
671 (Tong et al., 2007). The silty clay loam soil (pH of 6.9, OM content 4%) was incubated with each of
672 the nanoparticle treatments for 180 d (Tong et al., 2007). Both C_{60} and nC_{60} resulted in limited
673 alteration to either the function or structure of microbial processes or communities (Tong et al.,
674 2007). These findings are similar to those of Johansen et al. (2008), and consistent with other
675 investigations in which the bioavailability and antibacterial activity of nC_{60} reportedly diminished
676 following sorption to soil, with the overall sorption capacity dictated by the soil OM content (Li et
677 al., 2008).

678 Despite differences in experimental setups between the studies by Johansen et al. (2008) and
679 Tong et al. (2007), from the data presented, it is not possible to rule out the bioaccessibility and
680 toxicity of C₆₀ to a proportion of microbiota within soils. Although alterations to microbial
681 respiration as a result of fullerene addition to soil were not observed in either study, functional
682 substitution of specific impaired microorganisms may have occurred, masking any apparent
683 variation (Ekelund et al., 2003; Johansen et al., 2008). The studies presented here provide credible
684 insight into the possible toxicity of CNMs within the environment; however, insufficient data
685 comparatively analysing the impact of all CNMs on microbial populations within a range of well-
686 defined soil types is a major obstacle in determining their potential environmental impact.
687 Experimental work aimed at addressing the real world implications for particle toxicity to different
688 microbial communities, systematically testing the factors determining the behaviour and fate of
689 CNMs in soils highlighted previously, is required before firm conclusions can be drawn regarding
690 the impact of CNMs on soil microbial activity and structure. Specifically, the implications of abiotic
691 alterations and methods of CNM preparation on the bioaccessibility and toxicity to soil microbiota
692 have received little investigation.

693 *5.3 The bioavailability and bioaccessibility of CNM associated contaminants*

694 Sorption of contaminants is a fundamental mechanism in the regulation of organic
695 compound bioavailability (Lou et al., 2011). Given their strong sorptive capability, the addition of
696 CNMs to soil may result in the sequestration of organic contaminants, reducing their extractability
697 and bioaccessibility, operating in a similar manner to hard or black carbon (Chen et al., 2007).
698 However, the extent to which the processes identified in Section 4.1 impact upon the
699 bioaccessibility of contaminants and biodegradation have not received much research within soils.

700 The conditions under which CNMs enter the soil are also critical to determining their impact
701 upon contaminant bioaccessibility. Zhou et al. (2013) incubated ¹⁴C-2,4-dichlorophenol (¹⁴C-2, 4-
702 DCP) in a soil containing either 0, 2, 20 or 2000 mg kg⁻¹ SWCNTs or MWCNTs to determine the
703 impact of carbon nanomaterials on the mineralisation, degradation and distribution of ¹⁴C-2-4-

704 DCP in the soil. The impact of the order in which the nanomaterials were added to the soil was
705 also assessed, with nanomaterials added either after spiking, simulating disturbance of CNTs on
706 pre-existing contamination in soils, or as a mixture with ¹⁴C-2, 4-DCP, simulating HOC degradation
707 when carried or accumulated (concentrated) by CNMs within the environment from other
708 sources. CNTs added at concentrations $\leq 20 \text{ mg kg}^{-1}$ after spiking resulted in no significant effects
709 on the time course of mineralisation, indicating that the activity of microorganisms was not
710 significantly influenced, nor did the desorption from CNTs reduce ¹⁴C-2, 4-DCP bioavailability in
711 soil (Zhou et al., 2013). However, following the addition of CNTs at 2000 mg kg^{-1} added after
712 spiking, mineralisation of ¹⁴C-2, 4-DCP was significantly ($P < 0.05$) inhibited, which was attributed
713 to a reduction in the aqueous phase concentration of ¹⁴C-2, 4-DCP in soil solution by 1/5 and 1/12
714 for SWCNTs and MWCNTs, respectively (Zhou et al., 2013). CNT interactions with contaminants
715 within the soil environment due to aggregation therefore reduced available sorption sites, as well
716 as aggregate interaction with soil components such as humic substances, DOM, peptone and TA,
717 which potentially coat CNTs modifying surface polarity, reducing surface area and hence reducing
718 HOC sorption capacity as discussed in Section 4.1 (Wang et al., 2008b; Cui et al., 2011; Zhou et al.,
719 2013). As the adsorption of ¹⁴C-2, 4-DCP to CNTs was reversible, the bioaccessibility of 2, 4-DCP
720 was not reduced; however, indigenous microorganisms were not able to mineralise desorbed ¹⁴C-
721 2, 4-DCP at the same rate of desorption due to the possible toxicity effects of CNTs on microbial
722 activity (Zhou et al., 2013). CNTs are therefore potentially able to increase the persistence of
723 organic pollutants within soil through reducing biodegradation, with greater effects observed for
724 pre-adsorbed contaminants (Zhou et al., 2013). However, it is possible to speculate about the
725 environmental relevance of the investigation, as a concentration of 2000 mg kg^{-1} is likely several
726 orders of magnitude higher than could realistically be assumed to exist (outside of localised 'hot-
727 spots') within the environment (Zhou et al., 2013).

728 Similar results were obtained by Cui et al. (2011). Sediments (20 g) were first amended with
729 either biochar (100 mg), charcoal (20 mg) or SWCNTs (20 mg), then spiked with phenanthrene

730 | ~~(0.50 mg kg⁻¹). The mineralisation of phenanthrene, who assessed the bioavailability of~~
731 | ~~phenanthrene to microorganisms by *Mycobacterium vanbaalenii* PYR1) in sediments amended~~
732 | ~~with either SWCNTs, biochar or charcoal, with mineralisation was inhibited by 40.3 + 1.5, 40.5 +~~
733 | ~~2.6 and 29.5 + 3.5% for biochar, charcoal or SWCNTs, respectively. to the greatest extent by~~
734 | ~~SWCNTs.~~ It was proposed that the larger surface area and pore volume of SWCNTs relative to the
735 | other sorbents was responsible for the ~~observed results~~ reduced phenanthrene mineralisation.
736 | However, following the coating of SWCNTs with either HAs, TAs or peptone, a reduction in
737 | phenanthrene sorption occurred due to reduced pore volumes and surface area, ultimately also
738 | reducing the extent to which sorption to SWCNTs reduced mineralisation (Cui et al., 2011).

739 | In addition to the impact of soil types on the impact of CNMs on organic contaminant
740 | sorption, properties of the organic chemicals within soils are also influential in dictating their
741 | interaction with different types of CNMs. Towell et al. (2011) assessed the impact of fullerene
742 | soot (FS), SWCNTs and MWCNTs at 0, 0.05, 0.1 and 0.5% concentrations, on the HPCD
743 | extractability (proven as an indicator of PAH bioaccessibility to soil micro flora (Reid et al., 2000;
744 | Doick et al., 2005; Stokes et al., 2005; Rhodes et al., 2008b) and mineralisation of ¹⁴C-
745 | phenanthrene, and HPCD extractability of ¹⁴C-benzo[*a*]pyrene (¹⁴C-B[*a*]P) in soils over an 80 d
746 | period. Soils were first amended with CNMs, and then spiked with the contaminant. At
747 | concentrations ≥ 0.05% CNMs, ¹⁴C-phenanthrene mineralisation was significantly inhibited,
748 | suggesting enhanced PAH sorption reduced the aqueous substrate available for microbial
749 | mineralisation (Towell et al., 2011). Differences were also apparent between CNM types, with
750 | SWCNTs generally resulting in greater mineralisation inhibition in relation to MWCNTs and FS
751 | (Towell et al., 2011). However, at a concentration of 0.5% CNMs, ¹⁴C-phenanthrene was
752 | mineralised to a greater extent with SWCNT amendments than FS. This disparity was attributed to
753 | variation in rates of phenanthrene desorption from the solid to aqueous phase, as desorption
754 | hysteresis occurs more commonly with fullerenes than CNTs due to differences in aggregate
755 | structure and availability of sorption sites (Cheng et al., 2005; Yang and Xing, 2007; Towell et al.,

756 2011). The HPCD extractability of ¹⁴C-phenanthrene was significantly reduced as a result of CNM
757 amendment in a concentration dependant manner due to increased numbers of sorption sites
758 resulting in enhanced phenanthrene sorption (Towell et al., 2011). However, while the HPCD
759 extractability of ¹⁴C-B[α]P reduced with increasing concentrations of SWCNTs and MWCNTs, no
760 significant concentration dependant differences were observed with FS (Towell et al., 2011). The
761 ability of CNMs to sorb and hence modify the bioaccessibility of HOCs is therefore dependent on
762 the differences in physicochemical properties of the PAH in relation to the properties of the CNM.
763 However, the study did not consider possible differences in the toxicity CNMs between particle
764 types when discussing variations in mineralisation trends.

765 When considering the fraction of contaminants sorbed to CNMs within these investigations,
766 and the resulting reduced bioavailability, two schools of thought may be adopted; (i) over time
767 the non-degradable, bound fraction may innocuously degrade (Gevao et al., 2000a), or (ii) the
768 bound fraction is potentially re-mobilised over long time scales with potential environmental
769 implications (Gevao et al., 2000b). This draws on the discussion by Semple et al. (2013), in which
770 the significance of distinguishing between bioavailability and bioaccessibility is significant,
771 particularly when dealing with environmental 'super sorbents' such as CNMs with reference to
772 remediation of contaminated land and risk assessment. Semple et al. (2004) defined
773 bioavailability as 'that which is freely available to cross an organism's cellular membrane from the
774 medium the organism inhabits at a given time', and is considered as a rate of substrate delivery to
775 cells. While bioaccessibility encompasses this fraction, it additionally extends to those which are
776 potentially available over time, but are currently chemically or physically removed from the
777 microorganism (Semple et al., 2004). In other words, it provides a definition of the total extent of
778 substrate that will be available to cells. Arguably, bioaccessibility is of relatively greater
779 importance when considering the fate and behaviour of CNM sorbed contaminants, due to the
780 larger temporal range and lack of implied immediacy. However, under some environmental

781 conditions, microbial colonisation of CNM agglomerates can occur, with potential implications for
782 the bioaccessibility of the bound contaminant fraction.

783 *5.4 Microbial sorption and biofilm formation*

784 While the toxicity of CNMs in soil is dependent on their bioaccessibility in addition to
785 retention of reactivity, if agglomerates of CNMs are present with a reduced cytotoxic nature, it is
786 conceivable that interstitial gaps in the agglomerate with mesopore dimensions will result in their
787 increased suitability for the sorption of microorganisms (Agnihotri et al., 2005; Upadhyayula and
788 Gadhamshetty, 2010). When this is related to the previous discussion of CNM contaminant
789 sorption and the implications for biodegradation, it is possible to re-consider the lack of
790 bioaccessibility of CNM sorbed contaminants reported in some studies, and consider their
791 potential to increase contaminant bioaccessibility in certain situations. Properties of particular
792 importance when considering CNMs for such applications include: (i) structures with high
793 porosities readily colonisable by microorganisms; (ii) potential ability to encourage biofilm
794 formation through offering a buffering capacity and (iii) the ability to adsorb high concentrations
795 of contaminants from bulk solution yet regulate the microbial biodegradation through desorption
796 (Abu-Salah et al., 1996).

797 Biofilms are groups of well-organised, adjoining cells encapsulated within a matrix of
798 insoluble, extracellular polymeric substances (EPS) (Morikawa, 2006). EPS encapsulation supports
799 cell substance and growth through the trapping, binding and dissemination of external nutrients
800 by charged polysaccharide groups (Cheng et al., 2007), and offers greater protection against
801 external stresses within the environment relative to those residing in a planktonic state (Pang et
802 al., 2005). Materials that allow a high degree of bacterial colonisation and possibly biofilm
803 formation are potentially suited to facilitating biodegradation (Upadhyayula and Gadhamshetty,
804 2010), which is typically most effective when microorganisms are in biofilm state relative to
805 planktonic, due to greater bioavailability, protection and adaptability to toxic conditions and
806 hence more rapid pollutant degradation (Singh and Cameotra, 2004; Singh et al., 2006).

807 Furthermore, bacterial colonisation may stabilise nanoparticle aggregates, as polysaccharides
808 such as those generated by bacteria, have been observed to significantly increase the aggregation
809 of C₆₀ fullerene, reducing particle mobility within the environment (Espinasse et al., 2007).

810 Upadhyayula and Gadhamshetty (2010) conducted hypothetical calculations to determine
811 the quantity of cells that an agglomerate of CNTs could potentially sorb. The dimensions of a
812 typical bacterium such as *Shewanella oneidensis* (*S. oneidensis*) are 2 µm in height with a radius of
813 0.5 µm, resulting in a surface area of 7.85 x10⁻¹² m². Assuming that 10% of the surface area of 0.1g
814 CNTs added to media was available for bacterial sorption, the CNTs would be able to sorb 3.18
815 E+13 *S. oneidensis* cells (Upadhyayula and Gadhamshetty, 2010). Furthermore, Upadhyayula et al.
816 (2009) confirmed that the adsorptive capacity of nanotubes for the bacterial strain *Bacillus subtilis*
817 to be 37 times greater than the capacity of activated carbon; however, this may vary depending
818 upon pore volumes and surface area, which are key determinants of immobilisation capacity
819 (Upadhyayula and Gadhamshetty, 2010). Given these parameters, it is conceivable that biofilms
820 could develop on CNM aggregates given sufficient pore volumes and diminished CNM reactivity.

821 When the potential for biofilm development on CNMs is considered in relation to their HOC
822 sorptive ability and aggregation within soils, it has been suggested that CNMs may be useful for
823 enhancing biodegradation of organic pollutants that cannot be easily concentrated. With CNM
824 aggregates behaving as an organic chemical collector and accumulator, biofilm development on
825 CNMs potentially increases the bioavailability/bioaccessibility of the contaminant (Yang et al.,
826 2006b). Given adequate reversibility of organic compound adsorption and limited desorption
827 hysteresis, sorption of bacterial cells to the surface of CNM aggregates may shorten the diffusion
828 distance, facilitating the utilisation of the sorbed organic compound by the bacteria. This is well
829 illustrated by Yan et al. (2004), who studied the removal efficiency of microcystins (MCs) toxins
830 from solution by *Ralstonia solanacearum* bacteria (Gram-negative cells which are able to readily
831 coalesce on fibrous material) immobilised as a biofilm on a nontoxic form of CNTs. Their results
832 showed that the removal efficiencies of MCs were 20% greater by CNT biological composites than

833 either CNTs or bacteria alone (Yan et al., 2004). The findings were explained through absorption
834 of large amounts of MCs and *R. solanacearum* by CNTs, ~~even when the concentration of MCs was~~
835 ~~highly diluted in water~~, resulting in a concerted biodegradation reaction (Yan et al., 2004). In a
836 similar investigation, Kanepalli and Donna (2006) used CNT-bacteria nanocomposites to assess the
837 bioremediation of highly persistent trichloroethylene (TCE) in ground water. The study revealed
838 that TCE instantly sorbed to bacteria-nanocomposites, which was later released to bacteria that
839 were immobilised on the surface and metabolised.

840 Xia et al. (2013) studied the bioavailability and desorption (Tenax TA) of ¹⁴C phenanthrene
841 aged over 60 d with four different MWCNTs with varying surface areas in aqueous solution.
842 MWCNTs significantly ($P < 0.05$) reduced the mineralisation of phenanthrene in accordance with
843 their properties, with particles possessing larger specific surface areas together with large meso-
844 and micro-pore volumes resulting in the lowest mineralisation efficiencies. Bacteria were also
845 observed to colonise the surface of MWCNT aggregates, proportional to the quantity of
846 phenanthrene desorbed through Tenax TA extractions (Xia et al., 2013). Although slight changes
847 to the physical appearance of the bacteria were observed when sorbed to MWCNT aggregates,
848 potentially indicating a toxicity effect, the ability of the cells to metabolise phenanthrene sorbed
849 to low surface area particles may not have been significantly reduced (Xia et al., 2013). However,
850 the lack of a control sample in which the metabolism of cells under conditions devoid of CNMs
851 was assessed, limited the ability of the paper to determine the overall impact of MWCNT
852 aggregates on phenanthrene mineralisation.

853 Very little information is available on how CNMs act within soil matrices, especially in relation
854 to their adsorption to organic fractions, organic pollutants and their subsequent toxicity (Dinesh
855 et al., 2012). With an angelus sorbents such as black carbon (BC), elevated mineralisation of a
856 phenanthrene substrate has been observed as a direct result of BC addition to soil, which was
857 tentatively attributed to microbial sorption and utilisation of phenanthrene from the sorbed
858 phase (Rhodes et al., 2008a; Rhodes et al., 2012). Only one study has identified an increase in

859 contaminant mineralisation in soils following the addition of CNMs. Xia et al. (2010) studied
860 phenanthrene biodegradation and desorption characteristics (using XAD-2) in 21-40 day aged
861 MWCNT-amended soils relative to soils amended with wood char and black carbon. Following
862 each ageing interval, *Agrobacterium* (the degrading inoculum) was added to the soil, and the
863 contaminant degradation efficiency measured. After 28 and 40 days ageing, the degradation
864 efficiency in MWCNT-amended soils was 54.2% and 24.6%, respectively; wood char amended
865 73.5% and 25.1%, respectively and black carbon amended 83.8% and 38.3%, respectively. Thus a
866 reduction in bioavailability of contaminants sorbed to each of the sorbents with increasing soil
867 contact time is observed (Xia et al., 2010), together with the relatively low bioavailability of
868 contaminants sorbed to MWCNTs relative to other environmental sorbents. Desorption studies
869 identified similar residual concentrations of phenanthrene; however, during rapid stages of
870 degradation, desorption rates were found to under-predict the rate of degradation (Xia et al.,
871 2010). This potentially suggests that for each of the sorbents, phenanthrene was available to
872 bacteria either through the promotion of desorption or direct access (Xia et al., 2010).

873 Given the discussion above, it is possible to consider an additional factor to those proposed by
874 Kretzschmar et al. (1999) in Section 4, to determine the significance of contaminant facilitated
875 transport by CNMs. If the CNM sorbed contaminant is available to the cells through utilisation
876 from the sorbed phase, the importance of desorption of sorbed compounds from CNMs during
877 transport is reduced. It is therefore proposed that incorporation of a fifth factor, 'the
878 bioavailability and bioaccessibility of CNM sorbed contaminants to microorganisms from the solid
879 phase', may be appropriate, as inferring bioaccessibility through desorption investigations may
880 lead to incorrect assumptions. However, substantially more work is required to identify the exact
881 mechanism involved in these findings, and the specific conditions under which contaminant and
882 microbial sorption to CNMs could potentially result in toxicity from the CNM itself, from the
883 sorbed contaminant or both (Nowack and Bucheli, 2007). It is also possible that under some
884 environmental conditions, rapid desorption or excessive bioavailability of sorbed contaminants

885 may shock load sorbed bacteria and prove toxic (Upadhyayula and Gadhamshetty, 2010).
886 Biodegradation of contaminants sorbed to CNMs therefore still requires substantial investigation
887 into specific combinations of pollutants and microorganisms (Upadhyayula and Gadhamshetty,
888 2010), to determine whether the bioaccessibility of sorbed contaminants is either increased or
889 decreased, and if the addition of CNMs will increase the mobility of contaminants in the
890 environment. The general paucity of knowledge regarding the duration for which contaminants
891 will remain sorbed to CNMs requires addressing to determine the long-term stability of
892 contaminants sorbed to different nanoparticle types. Furthermore, the extent to which CNMs
893 influence the transformation residues of HOCs in soils such as bound residues formed during
894 organic pollution degradation in soil is unknown (Barriuso et al., 2008; Shan et al., 2011; Zhou et
895 al., 2013).

896

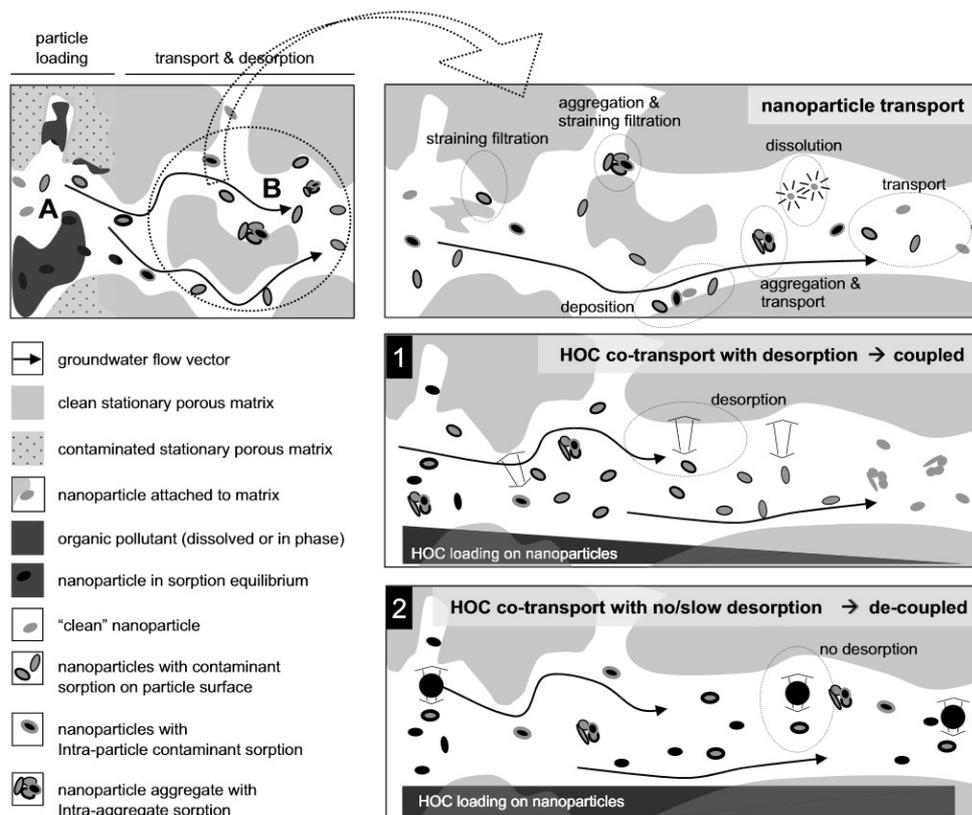
897 **6. Summary and conclusions**

898 The complex and dynamic nature of both soil environments and CNM physicochemical
899 properties generates enormous uncertainty in attempting to predict their behaviour and impact
900 on contaminant sorption, sequestration and transport as well as microbial interactions. This
901 review argues that the fate and behaviour of CNMs in soils is influenced by multiple parameters
902 such as the type and quantity of SOM, the type of clay particles present, the dominant charge
903 characteristics of the matrix as dictated by the soil inorganic fraction, together with properties of
904 the CNM, each of which is heavily influenced by pH and ionic strength. In addition, to a small
905 extent, biological activity has been shown to modify carbon nanomaterial fate. However,
906 presently only limited no research has been conducted into the manner in which each these
907 parameters-factors interact and collaboratively influence the fate and behaviour CNMs in real
908 environmental scenarios, is available and significantly more research is required.

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

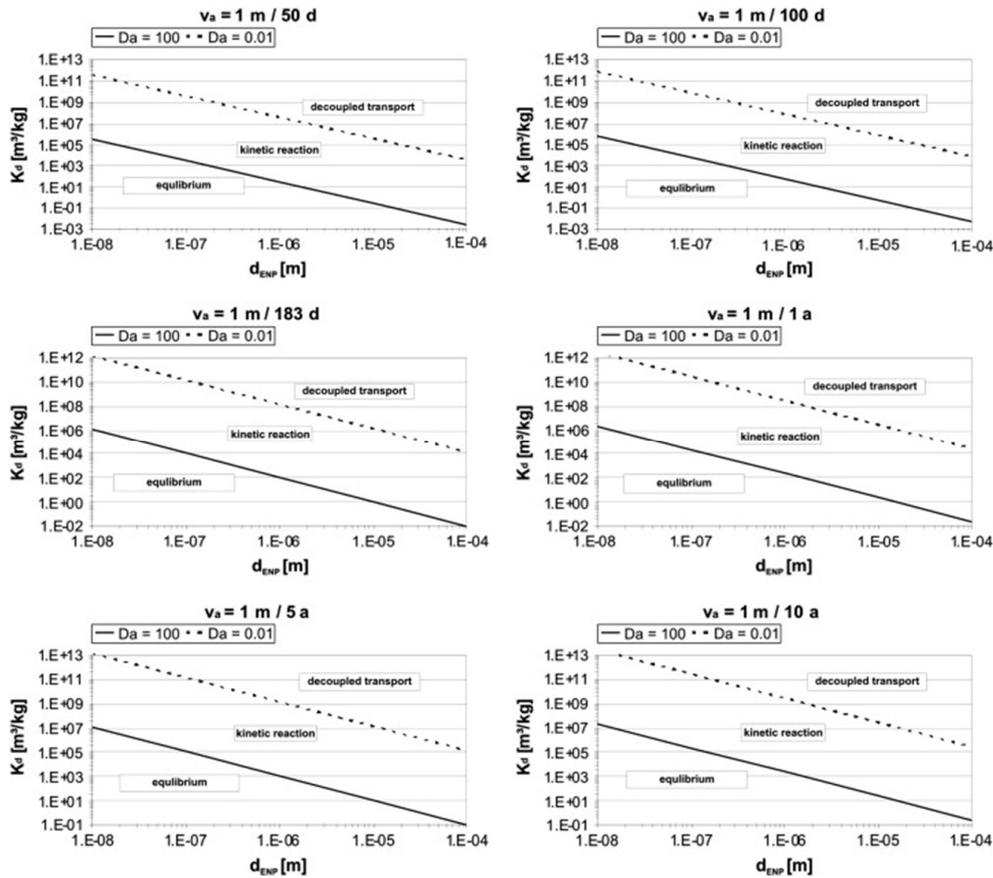
920 Finally, CNMs are undoubtedly efficient sorbents for a range of HOCs. However, while a
921 reduction in bioaccessibility of contaminants in soils has been demonstrated (Towell et al., 2011),
922 possibly indicating to uses as agents to land reduce bioaccessibility of contaminants, information
923 regarding sorption stability together with their potential to increase contaminant mobilisation
924 and other secondary effects are as yet too poorly developed to fully anticipate the possible
925 environmental impact. To determine the behaviour of CNMs within soils, it is concluded that no
926 one set of environmental or CNM characteristics can be viewed in isolation. Hence, given the
927 diverse array of variables, it is argued that risk-assessment of CNMs within the soil environment
928 should be conducted on a case-by-case basis. Detailed analysis of other environmental
929 compartments in which CNMs can potentially accumulate such as sediments, should also be
930 considered.

931



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

939 **Figure 2**



940

941 **Figure 2.** Simulation of diffusion limited desorption using of pore water velocities (v_a) between 1
 942 m/50 d to 1 m/10m/y. The solid line represents the Damköhler number of 100 (representing
 943 equilibrium transport above which the HOC will equilibrate between the CNM and soil matrix),
 944 the dashed line indicates a Damköhler number of 0.01 (decoupled transport below which HOC
 945 desorption will not occur within the timeframe of transport). If Damköhler numbers are < 100 or
 946 >0.01, kinetics of sorption should be considered in transport models (Hofmann and von der
 947 Kammer, 2009). Re-printed with permission from Elsevier, © 2014.

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