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Fate and bioavailability of engineered nanoparticles in soils: a review

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13 **ABSTRACT**

- 14 Interactions within natural soils have often been neglected when assessing fate and
- 15 bioavailability of engineered nanomaterials (ENM) in soils. This review combines patchwise
- 16 ENM research using natural soils with the much wider literature on ENM performed in
- 17 standard tests or on the fate of colloids in soils, and an analysis of the diverse ENM
- 18 characteristics determining availability from the soil organisms' perspective to assess the
- 19 main soil characteristics that determine the fate, speciation and ultimately bioavailability of
- 20 ENM in natural soils. Predominantly salinity, texture, pH, concentration and nature of mobile
- 21 organic compounds and degree of saturation determine ENM bioavailability.

22 INTRODUCTION

- 23 Nanomaterials are defined as natural, incidental or manufactured materials containing
- 24 particles, in an unbound state or as an aggregate or agglomerate, where \geq 50 % of the number
- size distribution show one or more external dimensions in the size range of 1 nm 100 nm.
- 26 Production of engineered nanomaterials (ENMs) has steadily increased due to new, beneficial
- 27 properties of ENM. This production increase is expected to also increase ENM emission into
- the environment (Benn and Westerhoff, 2008; Gottschalk and Nowack, 2011), an increase

29 that may be of concern because it is has been shown, predominantly in standard tests, that the 30 novel properties specific to some ENM may also lead to an increased toxicity, relative to bulk 31 materials (Scown et al., 2010). Based on the mode of application and on the physical chemical 32 properties of the ENM itself, ENMs possibly reach different environmental compartments 33 (air, soil, freshwater systems, etc.) directly via handling (e.g. application of nanopesticides) or 34 accidental release, indirectly via wastewater, sewage sludge or landfills (Gottschalk et al., 35 2009). Soil is a major environmental compartment that may be a final sink for ENMs. Recent 36 studies have shown that ENM can be toxic to soil organisms (Tourinho et al., 2012), but most of these assessments occurred using pristine ENM at higher concentrations than 37 38 environmentally relevant and in standard tests, often in artificial soils or in hydroponic 39 settings. The actual risk of an ENM exposure in a natural soil depends on the bioavailability, 40 which is the actual ENM concentration to which organisms are exposed to and which may 41 lead to effects (ISO17402, 2011). The bioavailable concentration of ENM is lower than the 42 total concentration in most realistic environments, particularly in soils, where there is a high 43 concentration of reactive surfaces with which the ENM can interact and a range of chemical 44 environments in which the "speciation" of ENM, i.e. their form of occurrence, can be 45 transformed before they reach an organism.

Both the organisms' perspective to bioavailability and the bioavailability as affected by soil 46 47 properties are critically analysed in this review. The soils properties determine all reactions 48 that determine the speciation and mobility of ENM in soils. Mobility is relevant in the context 49 of bioavailability because some organisms may perceive toxic substances and avoid exposure 50 to poorly mobile ENM that spread inhomogeneously in the soil profile (Fabian and Petersen, 51 1994; Mather and Christensen, 1998) and sessile organisms like plants will be reached much less by poorly mobile ENM. Few transport studies or toxicological assessments of ENM have 52 53 occurred in natural soils even though the widely varying chemical environments of natural

soils are likely to affect mobility, speciation and thus bioavailability in different ways. This review therefore sources the more extensive available literature on aquatic chemistry of ENM and transport of naturally occurring particles in natural soils to assess the potential influence of different properties of natural soils on ENM mobility and speciation in realistic environments.

59 The capability of different ENM species to interact with the biological interface, once the 60 ENM species have reached an organism, is bioavailability from the organisms' perspective. 61 The speciation of ENM in soils may comprise as-produced ENM, but probably more often 62 chemically transformed and/or aggregated ENM. The term "aggregate" is used in this review when referring to ENM clusters of any form. This wording is motivated by the strength of 63 64 adhesion of most ENM to each other and/or to other particles, by which ENM most often form aggregates rather than agglomerates that refer to a more loosely bound particle cluster 65 66 (Petosa et al., 2010).

Nanotechnology is a rapidly evolving field with the number and diversity of materials increasing exponentially. In addition, it will be argued in this review that ENM undergo many alterations while traveling from the point of emission to the soil compartment making both the fate and bio-availability of ENM pathway-dependent. Rather than focusing on a selected set of ENM, this review ventures a more general approach in an attempt to increase future relevance in the context of new materials, but also emerging research on environmentally altered materials.

74 EXPOSURE PATHWAYS OF ENM TO SOILS

The release of ENMs from point or diffuse sources, may take place as primary particles,
agglomerates, aggregates, embedded in a matrix or coated with different molecules and
substances (Nowack and Bucheli, 2007). Direct exposure pathways of ENM to soils occur

when ENMs are used as fertilizer (DeRosa et al., 2010), pesticides(Zhang, 2003), for
remediation of contaminated soils (Grieger et al., 2011) or accidental release. In these
instances, as-produced ENM, sometimes referred to as "pristine" ENM, enter the soil
environment.

82 The application of waste water treatment plant (WWTP) sludge is an important unintentional 83 ENM exposure pathway for agricultural soils (Gottschalk et al., 2009; Johnson et al., 2011), 84 because, on a mass basis, more than 90 % of silver (Ag), zinc oxide (ZnO), ceria (CeO₂), titania (TiO₂) ENMs or fullerenes (nC_{60}) spiked in to WWTP are retained within the sludge 85 86 (Doolette et al., 2013; Johnson et al., 2011; Kaegi et al., 2011; Kiser et al., 2009; Kuhlbusch et 87 al., 2012; Limbach et al., 2008; Tiede et al., 2010; Wang et al., 2012c; Westerhoff et al., 88 2011) and a similar partitioning is expected for carbon nanotubes (CNTs) (Petersen et al., 89 2011). WWTP sludge is used in some countries as land-amendment because of the high 90 organic content and high availability of nitrogen and phosphorus (Weggler-Beaton et al., 91 2003), thus unintentionally exposing soils to ENM.

92 ENMs in WWTP sludge are mostly aggregated with bacteria (Kiser et al., 2012; Kiser et al.,

93 2009; Limbach et al., 2008; Wang et al., 2012c), but ENM can also be associated with iron

94 oxides or other inorganic particles (Kiser et al., 2009) and/or, given the presence of humic

acids in WWTP sludge (Han et al., 2008), probably also coated with dissolved organic matter

96 (DOM). Exposure via WWTP can also have implications for the composition of ENM,

97 because Ag or ZnO ENM, for example, may react in WWTP with ubiquitous sulfide or

98 phosphate to form sparingly soluble Ag_2S , ZnS or $Zn_3(PO_4)_2$ nanoparticles (Doolette et al.,

99 2013; Kaegi et al., 2011; Lombi et al., 2012).

100 THE FATE OF ENM IN SOILS

101 ENM and colloids

102 Figure 1 shows the different processes determining the fate of ENMs in soils. Most of these 103 processes also determine the fate of colloids, i.e. naturally occurring particles in the 104 environment with a diameter smaller than 1 µm. The colloidal particle fraction comprises the 105 largest part of the potentially mobile particles in soils (Ryan et al., 1998). The much more 106 extensive research on the fate of colloids in soils provides an excellent starting point for 107 discussing ENM fate, given the overlapping size range. Moreover, the fate of ENMs and 108 colloids can be coupled because it will be argued that interaction between ENM and colloids 109 may be quantitatively important in many instances. The size of natural colloids ranges from < 110 30 nm for organic materials, whereas inorganic particles are usually larger than 20 - 30 nm 111 and are most likely iron and/or aluminium oxides or clays coated with these oxides and even 112 larger colloids (i.e. > 100 nm) are predominantly clays (e.g. illite, kaolinite, vermiculite), 113 carbonates often coated with organic matter, or bacteria (Chen and Beckett, 2001; 114 Claveranne-Lamolère et al., 2009; Geckeis et al., 2003; Perdrial et al., 2010; Ranville et al., 115 2005; Regelink et al., 2011).

116 Nanoparticle leaching

117 After WWTP sludge is ploughed into the soil, bacterial breakup and biological decomposition 118 of the organic material in the sludge likely result in resuspension of ENM aggregates from the 119 sludge matrix into soil pore water. This process may occur similarly to how mobile colloids 120 are suspended into the soil pore water as aggregates and/or individual particles by 121 hydrodynamic shear, e.g. during a rain event, a sudden drop in ionic strength (IS) (Grolimund 122 and Borkovec, 1999; Grolimund et al., 1998; Ryan and Elimelech, 1996), a redox change 123 where iron oxides that cement colloids together are reduced and dissolved (Henderson et al., 124 2012), or adsorption of ions such as phosphate (Ilg et al., 2008; Ryan and Elimelech, 1996) or

- 125 dissolved organic macromolecules (Kiser et al., 2012). Phosphate, amphiphilic proteins and
- 126 humic acids are ubiquitous in WWTP sludge and may increase interparticle repulsions
- 127 between ENM following adsorption (see further).

128 Homoaggregation

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory predicts that all ENM will eventually aggregate with each other, a process called homoaggregation. However, homoaggregation rates decrease if an electrostatic (or steric, see further) barrier hinders collisions between particles, to such an extent that the ENM suspension can be perceived as kinetically "stable", i.e. it is not observably aggregating within a subjectively set time-limit.

134 The extent of the electrostatic energy barrier varies with many environmental and particle-135 specific parameters; the most studied ones being pH and IS. Figure 2 shows predicted 136 homoaggregation rates of 20 nm TiO₂ (anatase) as a function of pH and IS. When protons are 137 the potential-determining ions, pH determines the magnitude of the surface potential of the 138 ENM and the IS determines the diffuse double layer (DDL) thickness, resulting in faster 139 aggregation the closer pH values are to the ENM's point of zero charge (PZC), i.e. the pH 140 where the net surface charge is zero, and the higher the IS up to an electrolyte concentration called the Critical Coagulation Concentration (CCC) where aggregation rates no longer 141 142 increase because they are limited by diffusion. Relatively small particles such as ENM have a 143 comparably small electrostatic barrier to begin with and therefore aggregate faster compared 144 to larger particles especially if the total concentration of particles is higher (Figure 2), which 145 has indeed been observed in most aggregation (and deposition) experiments (Elimelech and 146 O'Melia, 1990; Wang et al., 2012a).

Figure 3 shows that most literature CCCs of ENM homoaggregation are much higher than typical IS values of world soils. Homoaggregation in most non-saline soils will therefore likely be slow except when the pH is close to the ENM's PZC and/or when ENM number 150 concentration in pores are very high (Figure 2). When homoaggregation does occur, it most 151 often results in a reduced mobility of ENM in soils (Phenrat et al., 2009). Large aggregates 152 have larger drag coefficients resulting in an increased deposition (process 9 in Figure 1) 153 (Veerapaneni and Wiesner, 1996) and they experience more effects from straining (process 8) 154 in Figure 1) compared to individual particles. Darlington et al. (2009), for instance found that 155 differently sized aluminium oxide ENM had similar reduced mobility in a soil column, 156 because their aggregate sizes were similar and applications of high concentrations of 157 nanozerovalent iron (NZVI) for soil decontamination have so far been unsuccessful because 158 of the low mobility of aggregated NZVI (Phenrat et al., 2007; Saleh et al., 2008).

159 Heteroaggregation

160 Heteroaggregation is the aggregation of unlike particles, e.g. ENM with natural colloids or 161 other ENM. Studying heteroaggregation is much less accessible experimentally compared to 162 homoaggregation, but heteroaggregation most likely occurs more. Figure 2 compares 163 theoretical homoaggregation rates of anatase ENM with heteroaggregation of anatase with 164 colloids consisting of gibbsite or kaolinite, commonly found in soils. Theoretical 165 heteroaggregation rates appear to vary depending on the soil colloid with which the ENM 166 heteroaggregates but the rates appear higher in a wide pH - IS region compared to 167 homoaggregation rates, especially in the pH region between the PZCs of the ENM and natural 168 colloid. The surface charges of both particle types are opposite and interaction is *favourable* 169 in this pH region because of the absence of an electrostatic barrier preventing aggregation 170 (Kim et al., 2012a; Lin et al., 2005).

Heteroaggregation of ENMs is likely more often a quantitatively more important process of
ENM in soil pores compared to homoaggregation (Cornelis et al., 2012; Cornelis et al., 2010;
Cornelis et al., 2013; Hotze et al., 2010; Huynh et al., 2012; Kim et al., 2012a; Zhou et al.,
This hypothesis is supported by the much higher occurrence of heteroaggregates of

175 natural colloids in the environment compared to homoaggregates (Buffle et al., 1998) (Figure 176 4). ENM have often a negative surface charge, because commercial coatings or the adsorption 177 of negatively charged dissolved organic matter or anions such as phosphate induce a relatively 178 low PZC (see further). Table 1 gives an indication of iso-electric points and PZC values of 179 some common minerals in soils of which natural colloids are composed. An iso-electric point 180 is the pH value where the electrophoretic mobility is zero and can be considered a first 181 estimate of the PZC value. Note that many phyllosilicate clays (e.g. montmorillonite -182 kaolinite) have a different PZC value for the crystal planes or edges (Tombacz and Szekeres, 183 2006). Figure 2 suggests ENMs have a smaller pH-IS range of stability when in the presence 184 of particles with a different PZC compared to homogeneous ENM suspensions.

185 The role of heteroaggregation in the mobility of colloids or ENM has scarcely been studied.

186 Zhao et al. (2012c) observed simultaneous elution of ZnO ENM with Al and Fe from columns
187 of natural soils to which ZnO ENMs were added, suggesting colloid-mediated transport of

188 ENM. Heteroaggregation probably leads more often to a reduced rather than an increased

189 ENM mobility for the same reasons than when homoaggregation occurs (Cornelis et al., 2013;

Han et al., 2008; Kim et al., 2012a; Vasiliadou and Chrysikopoulos, 2011; Zhao et al., 2012c),

191 but both homo- and heteroaggregation may also lead to increased mobility, e.g. because of a

- 192 size-exclusion effect (process 7 in Figure 1). Hydutsky *et al.* (2007) found that adding
- 193 bentonite clay enhanced mobility of NZVI in a sand column, possibly by shielding the
- 194 positive charge on the surface of the iron, preventing it from depositing on negatively charged
- 195 sand grains.

196 Deposition

197 There is a chance, called the *collision efficiency*, that when a colloid or ENM approaches a

198 pore wall, that it will attach by Brownian diffusion or direct interception (process 9 in Figure

199 1), and/or by gravitational sedimentation (process 5 in Figure 1), collectively called

deposition. Brownian motion is most intense for relatively small particles such as ENM that
have a high diffusion coefficient, whereas interception occurs when the streamline of the
colloid or ENM encounters the pore wall or a large particle. Gravitational sedimentation
occurs predominantly with particles or aggregates larger than 1 μm (Elimelech, 1994;
Tufenkji and Elimelech, 2004).

205 The collision efficiency is in many cases determined by electrostatic interactions between the 206 depositing particle and the surface, similarly to aggregation. Favourable deposition occurs 207 when the repulsive barrier preventing deposition is low or absent (i.e. collision efficiency \approx 208 1). This may occur in the case of hydrophilic ENMs at IS values near the Critical Deposition 209 Constant (CDC). The CDC is a characteristic of a specific particle-surface combination that is 210 analogous to the CCC for the case of homoaggregation. Favourable deposition may also occur 211 when the particle and surface are oppositely charged in much the same way as favourable 212 heteroaggregation. In the case of carbon-based ENM materials, hydrophobic interactions can 213 also be important, e.g. leading to favourable deposition for non-functionalised CNT (Petersen 214 et al., 2011; Wang et al., 2010). The large aspect ratio of CNT also leads to relatively higher 215 deposition rates compared to colloids or other ENMs (Jaisi and Elimelech, 2009; Wang et al., 216 2012b), possibly because the CNTs can coil around soil particles (SedImair et al., 2012).

217 There is emphasis on considering deposition rather than homoaggregation as a mechanism in 218 most current models for colloid and ENM transport in soils. This is, at least partly, justified 219 because deposition rates of particles often appear higher compared to homoaggregation rates 220 of these particles (Chen and Elimelech, 2006; Grolimund et al., 2001; Gutierrez et al., 2010; 221 Kretzschmar and Sticher, 1997). However, Figure 2 suggests the aggregation rate of ENM 222 with natural colloids should decrease as the size of the colloid increases. If deposition is 223 considered analogous to aggregation of a relatively small ENM with a much larger colloid, 224 deposition should be similarly important than homo- or heteroaggregation. However,

225 deposition is very often more favourable than calculated based on macroscopic

measurements. The discrepancies are usually attributed to unaccounted surface roughness and
charge heterogeneity that are more pronounced for large surfaces than on small particles.
(Elimelech, 1994; Kretzschmar and Sticher, 1997; Petosa et al., 2010; Ryan and Elimelech,
1996).

230 Table 2 gives an overview of the few studies that have used natural soil materials or at least 231 no homogeneous quartz sand columns during retention and/or transport tests. A general 232 observation is that ENM retention is always higher in natural soils than in homogeneous 233 materials and higher than comparably larger colloids in similar conditions. Natural soils are 234 far more heterogeneous and complex and may, for instance, have localised patches of positive 235 charge, varying in size from < 10 nm to several μ m (Coston et al., 1995; Swartz et al., 1997), 236 predominantly originating from aluminium or ferric oxide coatings, but also clay edges 237 (Alonso et al., 2009; Chen et al., 2001; Kim et al., 2012a). Negatively charged ENM deposit 238 favourably on such small sites, whereas larger, negatively charged natural colloids only 239 encounter the average surface charge, most often negative in soils (Petosa et al., 2010). In 240 addition, smaller ENM are most likely less efficiently blocked from depositing on surfaces by 241 other particles already deposited on the surface, because small particles can easily fill the 242 "voids" left by previously deposited particles, whereas larger particles are blocked because 243 deposited charged particles alter the surface charge making deposition less favourable 244 (Semmler et al., 2000). Finally, inorganic ENM are often composed of materials, e.g. Ag, Au, 245 ZnO, with higher densities than natural colloids. More dense materials generally have 246 relatively higher Hamaker coefficients (Figure 5). Particles with high Hamaker coefficients 247 experience higher Van der Waals attraction to each other or towards dissimilar particles or 248 surfaces, increasing the chances of aggregation or deposition.

249 Straining, size exclusion and transport in unsaturated soils

250 When high removal of ENM is observed in soil columns despite high elektrokinetic barriers 251 normally preventing deposition, *straining* is often suggested, a process that involves physical 252 entrainment of particles independent of solution chemistry (Process 8 in Figure 1) (Bradford 253 et al., 2005; Bradford et al., 2003; Tufenkji et al., 2004). While, straining is thought to be 254 significant only below a particle size to average grain diameter ratio of 0.02 (Bradford et al., 255 2003), it is believed to occur at lower ratios also because of the roughness of soil particles 256 (Tufenkji et al., 2004) or because ENM gain access to the space inside larger soil aggregates 257 (Sagee et al., 2012). When the ENM aggregate size increases because of homoaggregation 258 (Solovitch et al., 2010) or heteroaggregation (Cornelis et al., 2013), the probability of 259 straining increases as well.

260 Large colloids or colloid aggregates that are excluded from smaller pores are transported only 261 in the much less tortuous larger pores (Grolimund et al., 1998). Size exclusion as a fate 262 mechanism for ENM has been suggested if access to inter-aggregate space is denied (Sagee et 263 al., 2012), although it is unclear how this mechanism occurs, or if prior homoaggregation 264 (Solovitch et al., 2010) or heteroaggregation (Cornelis et al., 2013) occur. It has also been 265 observed that transport of viruses, of which the size is also < 100 nm and that also have a 266 surface potential, was accelerated after heteroaggregation with kaolinite clays, because of size 267 exclusion (Walshe et al., 2010). Size exclusion is more pronounced in intact soil cores where 268 a significant proportion of the soil pore volume consists of macropores.

Soils are most often unsaturated, i.e. the soil pore volume is only partially filled with water.
Macropores are the first to be devoid of water; hence aqueous transport in unsaturated soils is
restricted to small, tortuous pores. In addition, particles are not only retained at solid-water
interfaces in unsaturated soils, but also at air-water and air-solid interfaces (Bradford and
Torkzaban, 2008; Crist et al., 2005), a phenomenon that reduces the mobility of most ENM,

but in particular organically coated colloids (Morales et al., 2011a; Morales et al., 2011b). The
more complex hydrodynamic conditions also increase the likelihood of straining (Bradford et
al., 2003).

277 Interactions with dissolved organic matter

278 Dissolved organic matter (DOM) is ubiquitously present in soil pore waters, reaching up to 1-100 mg L⁻¹ (Scheffer et al., 2004). The adsorption of DOM to the ENM surface significantly 279 280 alters its physicochemical characteristics and therefore its behaviour in the environment. 281 Important DOM in soils are humic and fulvic acids stemming from biomass degradation 282 processes, but intermediate degradation products or exudates from soil organisms such as 283 smaller acids or biopolymers (proteins, polysaccharides) may also interact with ENMs (Chen 284 et al., 2007). Anthropogenic sources of macromolecules are organic fertilizers or WWTP 285 sludge.

286 **DOM adsorption**

287 Soil organic matter can be divided in dissolved organic matter (DOM) and solid organic 288 matter (SOM). Adsorption of DOM to inorganic ENM surfaces occurs predominantly through 289 ligand exchange with surface hydroxyl groups of the DOM (Yang et al., 2009), by hydrophilic 290 interactions with other adsorbed functional groups (Chen et al., 2010; Hyung et al., 2007; 291 Schwyzer et al., 2012) or by hydrophobic π - π interaction with aromatic groups of DOM in the 292 case of carbon based ENMs such as CNTs or fullerenes (Hyung et al., 2007; Sedlmair et al., 2012; Yang and Xing, 2009). DOM adsorption to hydrophilic ENM is favourable at pK_{a,DOM} 293 294 $< pH < PZC_{ENM}$ because negatively charged DOM adsorbs more strongly to positively 295 compared to negatively charged ENM surfaces (Chen et al., 2012a; Chen et al., 2007), but 296 DOM is more protonated as the pH is lower (Gustafsson, 2001) making adsorption to 297 positively charged ENM surfaces less favourable. The adsorbed DOM concentration increases 298 with higher DOM concentration as well as with increasing IS (Chen et al., 2012b). It is

unclear whether DOM replaces or overlays existing coatings on ENM (Nason et al., 2012;
Stankus et al., 2011; Thio et al., 2011), but it appears that adsorbed natural DOM dominates
the surface properties rather than the original coating in most cases (Stankus et al., 2011;
Zhang et al., 2009). Following DOM adsorption, the PZC of the ENM surface will almost
always be shifted to lower values (Figure 6), because the surface potential at a given pH
becomes more negative.

Stabilisation by DOM

306 Figure 7 gives an overview of possible effects of DOM on nanoparticle aggregation rates. A 307 similar figure can be drawn for the effects of DOM adsorption on deposition. DOM 308 adsorption most often makes the surface potential of ENM more negative, a process that can 309 lead to a reduction in aggregation and deposition rates (Buffle et al., 1998; von der Kammer et 310 al., 2010; Zhang et al., 2009). When the surface charge of originally positively charged ENM 311 changes to the opposite sign in this process, favourable heteroaggregation or deposition to 312 predominantly negatively charged soil minerals is inhibited (Chen and Elimelech, 2008; 313 Huynh et al., 2012; Li et al., 2010; Tombacz et al., 2004). It should be noted that adsorption of 314 anions such as phosphate that are ubiquitous in agricultural soils, especially after a WWTP 315 sludge application, causes similar effects (Cornelis et al., 2011; Darlington et al., 2009) and 316 competes with DOM for adsorption (Hiemstra et al., 2010), while calcium can have the 317 opposite effect on negatively charged ENM (Schwyzer et al., 2012). DOM adsorption can 318 also lead to steric stabilization, especially for humic acids that are relatively rigid molecules 319 because of their high aromatic content (Saleh et al., 2010). Sterically stabilised systems are 320 much less affected by increased IS compared to electrostacitcally stabilised systems. Carbon-321 based ENM are particularly stabilised by DOM because their hydrophilicity is increased by 322 the acidic functional groups of the DOM (Petersen et al., 2011; Petosa et al., 2010).

Destabilisation by DOM

324 Adsorption of DOM can also lead to a destabilisation of ENMs (Figure 7) (Chowdhury et al., 325 2012; Nason et al., 2012). Bridging flocculation occurs if segments of a polymer adsorbed to 326 one particle become attached to other particles. This process occurs mainly for polymers 327 which are large enough to have free segments outside the zone of electrostatic repulsion and 328 was therefore predominantly observed for rigid biopolymers (Buffle et al., 1998). 329 Hydrophobic interactions can also lead to bridging flocculation and this effect does not so 330 much depend on the length of the molecules but more on the hydrophobicity of the adsorbed 331 DOM, usually correlated with the aliphatic carbon content (Nason et al., 2012; Wilkinson and 332 Reinhardt, 2005). Fewer polymer molecules are required to attain the bridging effect at higher 333 IS so bridging flocculation is more pronounced at higher IS (Wilkinson and Reinhardt, 2005). Divalent ions such as Ca²⁺ are more likely to aid in bridging flocculation to adsorbed DOM, a 334 335 phenomenon suggested by the so-called divalent cation bridging theory (Chen and 336 Elimelech, 2007; Jiang et al., 2013; Stankus et al., 2011; Wang et al., 2011a). The surface 337 coverage with adsorbed polymer appears an important factor for the bridging, where more 338 flocculation occurs at half surface coverage (Illes and Tombacz, 2006; Wilkinson and 339 Reinhardt, 2005) (Table 3). Adsorption of negatively charged DOM on a positively charged surface can also lead to charge neutralization and thus destabilisation of the ENMs. This 340 341 effect is concentration- dependent and stabilisation is observed at lower or larger coverage (Buffle et al., 1998; Wilkinson and Reinhardt, 2005). 342

343 **DOM in soils**

Most knowledge on ENM – DOM interactions stems from water phase studies. Extrapolation of these results towards soils requires caution. Soil HA, for instance, have more aromatic and less aliphatic structures in comparison to aquatic HA (Akaighe et al., 2011). A higher steric stabilisation is therefore expected in soils compared to aquatic media (Figure 7). DOM 348 adsorption indeed often leads to increased ENM transport in soils, mostly because of steric 349 stabilisation (Table 3). Electrostatic stabilisation is significant when ENM are positively 350 charged and DOM adsorption causes a charge reversal, because in most cases, soil minerals 351 are predominantly negatively charged (Jones and Su, 2012). The presence of DOM can also 352 increase the mobility of negatively charged ENM following adsorption of DOM to positively 353 charged heterogeneities on soil minerals, making deposition and/or heteroaggregation less 354 likely (Wang et al., 2010). Adsorption of DOM on top of existing ENM coatings is also 355 important, as commercial coatings by themselves may prevent homoaggregation, but not 356 necessarily also heteroaggregation or deposition (Lin et al., 2012). Table 3 also shows that the 357 presence of DOM may also reduce ENM mobility. Possible explanations are bridging 358 flocculation possibly enhanced by divalent cation bridging (Figure 7). The interaction 359 between ENM and solid organic matter (SOM) is poorly studied, but is unlikely to lead to 360 increased transport. Bacterial biofilms, for instance, retard ENM transport in sand columns 361 (Jiang et al., 2013; Xiao and Wiesner, 2013). C-based ENM preferentially interact with 362 organic (hydrophobic) surfaces and SOM will thus serve as a solid surface in much the same 363 way as e.g. negatively charged clays.

364 Dissolution and transformation

365 Most fate studies on ENM used pristine materials but recent studies show that the chemical 366 nature of these materials changes in the environment, e.g. after being released from nano-367 enabled products. Dissolution is the most widely investigated transformation reaction, possibly because the solubility of particles theoretically increases as their size decreases, 368 369 which has been experimentally verified for Ag and ZnO ENM (Liu et al., 2009; Miao et al., 370 2010; Zhang et al., 2011). However, the effect of size on dissolution rate in a realistic 371 environment, even for relatively soluble ENM such as Ag, ZnO or quantum dots, is probably 372 confounded by simultaneous deposition, aggregation, coating by organic matter and/or transformation to sparingly soluble materials. Ions dissolved from ENM are often adsorbed by soil particles or complex with chelating agents, which may accelerate ENM dissolution and/or transformation (Cornelis et al., 2012; Navarro et al., 2011). The dissolution rate of less soluble ENM such as CeO_2 ENM is most likely not significantly enhanced in natural soils and these ENM therefore likely accumulate if not leached out of the soil (Cornelis et al., 2011).

378 Relatively soluble ENM are often transformed to thermodynamically stable compounds in a 379 range of environments (Levard et al., 2012; Liu et al., 2011; Lombi et al., 2012; Lv et al., 380 2012; Milani et al., 2012; Misra et al., 2011). As described earlier, Ag transforms into Ag₂S 381 in WWTP forming Ag₂S nanoparticles of a similar size than the original Ag ENM and this 382 process occurs independently of the original Ag ENM coating (Lombi et al., 2013). A similar 383 process occurs also in soils (Lowry et al., 2012). Other ENM such as ZnO may lose their 384 nanoparticle character during transformation. Lombi et al. (2012) for instance found that 385 during aging of ZnO or ZnS containing sewage sludge, most Zn became associated with iron 386 oxides, a process that may also occur in soils. Biodegradation of carbon based ENM in soils is 387 possible, but scarcely studied and half-lives are likely to vary depending on locally available 388 enzymes in soil pores (Petersen et al., 2011).

389 Not only the core material of ENM is changed over time in soils, but most likely also the 390 coating. Small, electrostatically adsorbed organic acids such as citrate are easily degraded in a 391 range of environments, but even covalently bound large coatings can be degraded (Kirschling 392 et al., 2011). Such degradation possibly occurs abiotically by oxidation combined with 393 dissolution (Auffan et al., 2010; Labille et al., 2010), but it has been proposed that reactive 394 oxygen species that are naturally produced in soils, by e.g. fungi, can also mediate coating 395 degradation (Navarro et al., 2011). The decomposition of coatings likely results in reduced 396 ENM mobility in soils unless the coating is replaced by naturally occurring NOM according 397 to earlier explained mechanisms (Labille et al., 2010).

BIOAVAILABILITY OF ENM FROM THE SOIL ORGANISM'S PERSPECTIVE

399 *Modification of bioavailability by organisms*

400 Upon reaching organisms, ENM may be transformed further because soil organisms often 401 affect local physical chemical conditions and introduce enzymes and chelating agents, e.g. in 402 the intestines of invertebrates or in the soil rhizosphere near plant roots. These conditions may 403 affect the transformation and (local) bioavailability of ENMs. The conditions in intestines of invertebrates have not been studied extensively, but appear to be highly species-specific and 404 405 in some cases quite different to the conditions in the soil (Table 4). The composition of the 406 rhizosphere, i.e. near plant roots, has been studied more. This environment has a different pH compared to the bulk soil (Grinsted et al., 1982; Shen et al., 2004) and it contains many low 407 408 molecular-weight organic compounds such as organic acids (e.g. lactic acid), amino acids, 409 sugars, and fatty acids that plants excrete to make nutrients more available (Garcia et al., 2001; Matsumoto et al., 1979; Mimmo et al., 2011; Van Hees et al., 2003; van Hees et al., 410 411 2005) (Table 5). These compounds are known to adsorb on ENM, a process that may accelerate ENM dissolution in the case of relatively soluble ENMs such as ZnO into Zn²⁺ that 412 413 is much more easily taken up by organisms compared to ZnO ENM (Zhao et al., 2012c). Soil 414 environments changed by organisms can also locally alter or remove the coatings of ENM 415 (Navarro et al., 2011).

416 Uptake of ENM by soil invertebrates

Much research has been done on nano- and microparticle uptake in mammalian cells or *in vivo* through the gut epithelium in the context of drug uptake. This research may not directly be applicable to soil invertebrates (Landsiedel et al., 2012), because of differences both in physiological and physico-chemical conditions in the gastrointestinal tract. For instance, most particle uptake in mammals occurs via Peyer's patches in the ileum (Hagens et al., 2007), which do not occur in invertebrates, and the pH in the mammalian stomach is very low in 423 comparison to the pH reported for isopods and earthworms (Table 4). However, mechanistic
424 investigations on ENM uptake in invertebrate guts are inexistent. Research on mammalian
425 models may thus shed some light on how nanoparticle properties determine particle uptake in
426 invertebrates.

427 There is on-going discussion on the mechanisms by which ENM may enter animal cells and 428 on the particle properties that make ENM more or less likely for uptake (Muñoz and Costa, 429 2012). Passive, non-specific transport mechanisms of ENM in intestines are diffusion or 430 persorption. Decreasing ENM size, increasing hydrophobicity and positive surface charge 431 generally promote diffusion across membranes (Geiser et al., 2005; Lin et al., 2006; Nel et al., 432 2009). Persorption of ENMs may occur via breaks at the top of the intestine vili (Volkheim et 433 al., 1968), via tight junction channels between enterocyte cells (Carr et al., 2012) or through 434 gaps created by extruding enterocytes (Hillyer and Albrecht, 2001). Persorption occurs more 435 rapidly for positively charged, smaller ENM (Hagens et al., 2007; Hillyer and Albrecht, 436 2001).

437 Endocytosis is another important process in the uptake of ENM in animal tissues. In the 438 intestinal tract this is mainly pinocytosis (uptake of fluids and dissolved/dispersed materials 439 by cells) and not phagocytosis (uptake of solid particles by cells) (Canton and Battaglia, 440 2012). Endocytosis is generally triggered by interactions between particles or aggregates and 441 membrane associated receptors (Canton and Battaglia, 2012), so the type of coating of the NP 442 is essential in this step. Unspecific endocytosis also occurs, which is more efficient for 443 positively charged ENM. However in both cases, the biocompatibility of the coating of the 444 ENM appears more important than the properties of the core particle (Canton and Battaglia, 445 2012; Kelf et al., 2010). The relationship between size of a NP and the efficiency of 446 endocytosis in uptake is not unidirectional, but often shows an optimum (20-50 nm radius) 447 because larger particles require non-specific slow uptake and smaller particles do not generate 448 enough cell responses (Canton and Battaglia, 2012; Kelf et al., 2010). Endocytosis of large 449 aggregates (up to 100 - 500 nm) of citrate capped Ag-ENMs in the gut epithelium was 450 observed in Nereis versicolor (Garcia-Aonso et al., 2011). Shape, i.e. the aspect ratio, of ENM 451 is also important for endocytosis, increasing aspect ratio decreased the rate of uptake of gold 452 nanomaterials in vitro (Chithrani et al., 2006). A modelling study showed that rod-shaped 453 particles may not be fully wrapped by the membrane during endocytosis, while completely 454 round shapes may not be wrapped at all (Decuzzi and Ferrari, 2008). Particles with 455 intermediate aspect ratios were indicated to be fully wrapped. Internalisation of ENMs with 456 relative high aspect ratios is also depending on the angle at which the ENM is attaching to the 457 cells. It was shown that the internalisation of polystyrene elliptic discs only occurred in case 458 macrophage cells attached to the major axis of the particles. In cases the macrophages 459 attached to the sides of the ENMs no internalisation occurred (Decuzzi and Ferrari, 2008). 460 Active passage and endocytosis demand for functioning cells and energy. It may be however

461 that ENMs exert toxic effects to intestinal cells (Cha et al., 2012), which may eliminate the 462 active uptake processes through which ENMs may enter the body. It may therefore be that at 463 relatively low level ENMs may be bioavailable to organisms through active uptake, but that at 464 high exposure concentrations the uptake may be absent or less.

465 Uptake of ENM by plants

Plants can accumulate ENMs although the routes of uptake are still not very well established (Ma et al., 2010). Plant cells contain a cell wall, which may affect the uptake of nanoparticles differently to the uptake in animals. Table A1 lists several studies on uptake of ENM by plants under different experimental conditions. In these studies it is discussed that the uptake of ENM may also be related to their specific uptake by the mycorrhizal fungi (Whiteside et al., 2009). C_{70} particles are relatively small (*ca.* 1 nm) and they can be accumulated relatively easily by plants by osmotic pressure, through pores in cell walls, by intercellular 473 plasmodesmata or by symplastic uptake (Lin et al., 2009). In a study on ZnO, it was 474 hypothesised that ZnO ENMs may be able to increase the permeability of plant cell walls by 475 creating holes and permeate into the cells through these holes (Lin and Xing, 2008). After 476 entering the cells, ENMs may be able to be transported between cells through plasmodesmata, 477 which were shown to be approximately 40 nm width (Tilney et al., 1991). Additionally, very 478 small ENMs can be accumulated quite easily via apoplastic pathways, but for larger particles 479 the chemical composition of the surface may be very important in driving the uptake. This is 480 often an interaction between the plants and the mycorrhizal fungi. Furthermore ENMs may 481 adsorb strongly to the roots thus exerting effects even without being actually taken up as 482 particle (Navarro et al., 2012). However, it should be noted that most information on this 483 adsorption is drawn from hydroponic exposures and the mobility of ENM in water may be 484 much larger in comparison to soil. Therefore the number of ENM absorbing to roots may be 485 much smaller in soil. Zhao et al. (2012c) showed that relatively small ZnO ENM aggregates 486 can reach the transport system of corn grown in natural soil.

487

Uptake of ENM by soil micro-organisms

488 Bacterial cell walls may be damaged upon contact with e.g. reactive oxygen species produced 489 by ENMs (Neal, 2008), after which ENMs may enter the bacteria. Positively charged particles 490 are more attracted to the negatively charged cell membrane and may therefore induce more 491 effects, as was shown for ZnO ENMs (Neal, 2008)). Similarly, hydrophobic particles are also 492 more likely to interact with cell membranes (Hwang et al., 2012). In addition to the uptake of 493 ENMs in bacteria and their adherence to bacteria, dissolving metal ENMs may exert their 494 effects mostly through the release of ions, for instance in the case of CuO ENMs and ZnO 495 ENMs (Rousk et al., 2012). Bacteria cannot accumulate ENMs via pinocyctosis, but for instance in Pseudosomas aeruginosa, pores of 5.3 to 9.4 nm were detected, which are used to 496 497 excrete proteins (Bitter et al., 1998). Hence, small ENMs may be able to enter bacterial cells

through such pores. Fungi in the rhizosphere can accumulate ENMs, as was shown by a studyon *Poa annua* and associated fungi, but uptake is coating-specific (Whiteside et al., 2009).

500 BIOAVAILABILITY AS AFFECTED BY SOIL PROPERTIES

501 The role of ionic strength

502 An increase in IS accelerates unfavourable deposition, heteroaggregation and, if the ENM 503 concentration is high homoaggregation is also enhanced. Aggregation, in turn, leads to 504 enhanced deposition and straining. Most studies in Table 2 thus show that ENM mobility is 505 lower in soils with a relatively high ionic strength. Fast colloid-mediated transport of large 506 ENM aggregates can occur by the process of size exclusion when a macroporous structure is 507 present (Solovitch et al., 2010), but such fast ENM transport will also not result in 508 homogeneous spreading of ENM in the soil profile. In addition, large aggregates are less 509 likely taken up by most of the aforementioned biological uptake mechanisms. An increase in 510 IS thus most likely decreases ENM bioavailability.

511 The role of dissolution

There are many indications that bioavailability and hence ecotoxicity correlates with the amount of ions released from ENM in the case of soluble ENM such as Ag, some quantum dots and ZnO (Kool et al., 2011; Li et al., 2011; Pace et al., 2010; Schlich et al., 2013; Shoults-Wilson et al., 2011a; Shoults-Wilson et al., 2011b). When there is no relationship between toxic effect magnitude and the bioavailable concentration of ions dissolved from ENMs in the pore water, a nanoparticle-specific effect must be assumed, an effect that depends on the *in-situ* speciation of the nanoparticle.

519 The role of pH

A relatively high pH most often leads to a higher ENM mobility, because ENM surfaces are
generally negatively charged. ENM have commercial coatings or are coated with DOM,

522 phosphate or other anionic compounds in soils. However, Table 2 shows that there is often no clear correlation between mobility and pH. A possible explanation is that many fate processes 523 524 that promote ENM mobility in soils are confounded by a pH increase. An example is 525 adsorption of anionic compounds that compete with hydroxyls for adsorption. Other fate 526 processes are indifferent to pH change such as favourable heteroaggregation or deposition that 527 are diffusion-limited and therefore do not depend on the ENM pH-dependent surface charge. 528 The pH can also vary throughout the soil, especially near organisms (Tables 4 and 5) where it 529 affects bioavailability by determining the extent of dissolution, e.g. by mediating oxidation 530 (Unrine et al., 2010).

531 *The role of texture*

532 Table 2 shows that ENM retention generally increases with a finer soil texture. Granulometric 533 clay, the finest texture fraction, is predominantly composed of iron- and aluminium oxides 534 and mineral clays, all of which have pH-dependent surface charges (Kretzschmar et al., 1999). 535 A preferential interaction of predominantly negatively charged ENM with clays, especially at 536 pH values lower than the PZC of minerals of granulometric clays may explain the limited 537 mobility of ENM in finer textured soils (Cornelis et al., 2012; Cornelis et al., 2011). 538 Heteroaggregation of ENM with mobile clays can increase the aggregate size of ENM, 539 making them less available to organisms. Bioavailability of ENM is therefore likely lower in 540 finer textured soils as observed by Shoults-Wilson et al. (2011b).

541 The role of DOM

542 The effects of soil DOM on ENM mobility vary with the DOM concentration, DOM type, IS

543 and/or concentrations of divalent cations and pH. Soil DOM often enhances the detected

544 ecotoxicity/accumulation (and thus also the bioavailability) by increasing the mobility of

545 ENM, but also by especially when the organic coating is bio-compatible (Navarro et al., 2008;

546 Wild and Jones, 2009; Zhao et al., 2012c).

547 The role of other soil properties

548 Positively charged ENM are generally more attracted to negatively charged cell membranes 549 and are therefore more bioavailable. However, Table 2 shows that such ENM are generally 550 poorly mobile in soils or are often coated with DOM or phosphate ions (Cornelis et al., 2011) 551 or with organic acids excreted in the rhizopshere or the gut of invertebrates. Ag nanomaterials 552 added to soil are likely to occur as Ag_2S nanoparticles and remaining Ag ENMs are quickly 553 dissolved (Cornelis et al., 2012) or transformed in to Ag₂S, especially in reducing conditions 554 (Lowry et al., 2012). Ag₂S formation has indeed been observed in wetland soils and it was 555 shown that Ag₂S accumulates in plants indicating that it is still bioavailable (Lowry et al., 556 2012). Reducing properties of waterlogged soils also reduce Fe-containing colloids, possibly 557 leading to less heteroaggregation as has been observed for colloid mobilisation in reducing 558 soils (Lowry et al., 2012). In addition, ENM are likely less mobile in unsaturated soils 559 because of the existence of air-water interfaces where particularly C-based ENM attach 560 (Morales et al., 2011b). Relatively narrow pores are filled with water in unsaturated soils 561 where the distance to the pore wall is relatively small and deposition is therefore on average 562 more likely compared to saturated soils.

563 The role of test conditions

564 Aggregation and hence bioavailability can be influenced by the application form used for soil 565 spiking. No difference in toxicity on Folsomia candida between spiking soil with ZnO using a 566 dry powder or suspension in soil extract was detected (Waalewijn-Kool et al., 2012). Spiking 567 using a dry powder or suspension in deionised water was compared for TiO₂ in experiments 568 with various test organisms (Hund-Rinke et al., 2012). Wet spiking resulted in stronger effects 569 than dry spiking, but the bioavailability of the particles appeared to be limited when highly-570 concentrated nanoparticle suspensions were used for wet spiking. The different results 571 between wet spiking using a suspension in soil extract and a suspension in water compared

dry spiking may be the result of the different ENMs (ZnO: ion releasing NP; TiO₂: stable NP)
or different aggregate sizes in the presence of NOM compared to deionised water.

574 Relatively low ENM concentrations likely occur in most realistic exposure scenarios of ENM 575 to soils. High concentration of ENM would only occur e.g. after a calamity or intentional 576 ENM application such as a nanopesticides. However, predominantly the latter scenarios are 577 reflected in ecotoxicological studies where relatively high ENM concentrations are often 578 applied. From the discussion above it is clear that homoaggregation likely occurs in such 579 scenarios, whereas heteroaggregation and deposition are more likely mechanisms in natural 580 soils with relevantly low ENM concentrations. Moreover, deposition of ENM sometimes 581 increase with ENM concentration because already deposited ENM may form preferential 582 interaction sites for new ENM (Godinez et al., 2013). These multiple interactions may hamper 583 the establishment of clear dose-response relationships of ENM, an observation that has to be 584 considered when the results are to be used for risk assessment. Experiments with pure quartz 585 columns for mobility studies or hydroponic exposures are only of limited relevance for 586 ecotoxicological risk assessments in real environments because interactions with natural 587 colloids or surfaces do not occur. This will not only cause a different mobility of ENM, but 588 also a different form of occurrence of ENM and thus an unrealistic assessment of its 589 bioavailability.

590 Techniques to assess bioavailability of ENMs

591 Measuring the total (number) concentration of ENMs in soils is currently not possible, but it 592 is also clear from the discussion above that the total ENM concentration would be a poor 593 measure of the bioavailable fraction of ENM. In those cases where the toxic mode of action of 594 ENMs occurs through metals dissolved from the ENM, assessment of ENM bioavailability 595 may rely on the well-studied methods available for assessing dissolved trace element 596 bioavailability. Stable and radioactive isotope dilution techniques, for instance, have been used with success to assess the labile or potentially bioavailable pool of trace cations andanions in soils (Kirby et al., 2012).

599 When the toxic mode of action of ENMs is not through dissolution, indirect techniques to 600 estimate the bioavailable fraction need development, but would most likely involve an 601 extraction step. Analysing extracts can benefit from the rapidly developing technology to 602 analyse very low ENM concentrations in complex fluids (von der Kammer et al., 2012) and 603 ENM occurs from the soil pore solution as altered by nearby organisms, e.g. in the 604 rhizosphere or the invertebrate gut. The essentially non-equilibrium processes governing the 605 fate of ENMs in soils would probably require a temporally resolved extraction procedure. A 606 wide range of extractants has been suggested for assessing the bioavailable fraction of 607 dissolved metals, but the tests are usually metal-specific and require careful calibration using 608 actual uptake experiments (GA, 1988). Such calibration has, to date, hardly been undertaken 609 in the case of ENM. One example found poor correlations between extractable fractions 610 (CHCl₃, EDTA and water) of metal oxide ENMs and the response of soil biomass (Antisari et 611 al., 2013).

612 **CONCLUSION**

613 It is a challenge to predict bioavailability of specific ENM in natural soils given the many 614 interactions of several properties with each other and with environmental conditions which 615 may act in a synergistic or antagonistic way. Moreover, some of these specific interactions 616 have been scarcely investigated, particularly the role of different DOM in direct uptake by soil 617 organisms and the availability of different forms of occurrence of ENM such as 618 heteroaggregates to organisms. However, some general trends can be deducted or 619 hypothesized from the above discussion. It appears that bioavailability of ENM to a particular 620 organism species is generally higher in saturated, coarsely textured soil where IS is low and 621 DOM concentration is high. ENM bioavailability is expected to be low in unsaturated, finely

- 622 textured soils, where IS is high and DOM concentration is low. It should be noted that
- 623 bioavailability may vary with different organisms that can have different routes of uptake and
- 624 have therefore different sensitivities towards contaminants. Quantitative modelling is required
- 625 to classify intermediate cases as analysing the relative importance of all fate reactions was
- 626 beyond the scope of this review. It must also be noted that challenging the general trends
- 627 outlined is this review with such models and with empirical evidence is essential.

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FIGURES



Figure 1: Schematic overview of the main fate-determining parameters of colloids and ENM in solid matrices. 1. Colloid generation. 2. ENM leaching from biosolids. 3. Homoaggregation. 4. Fragmentation. 5. Sedimentation. 6. Heteroaggregation. 7. Size exclusion. 8. Straining. 9. Deposition. 10. Convective transport



Figure 2: log(frequency) histogram of world soil ionic strength values as a function of soil pH. Data from (FAO/IIASA/ISRIC/ISSCAS/JRC, 2012). The IS was calculated from the measured electrical conductivity in a saturated paste using an empirical transfer formula.(Gillman and Bell, 1978). Literature Critical Coagulation Concentrations (CCC) as a function of pH are also shown. A difference is made for CCCs obtained using salts monovalent or divalent cations, from which the corresponding IS was also calculated. There is also a difference made between studies that used uncoated or coated – natural or commercial – ENM.



Figure 3. Theoretical homo- and heteroaggregation rates (i.e. the decrease in number concentration of single particles as a function of time) of anatase ENM in different scenarios. Darker gray shades indicate 10 logaritmic units lower aggregation rates. Surface charge densities were calculated using Gouy-Chapman theory using intrinsic surface acidity constants from the literature (Kretzschmar et al., 1997; Weerasooriya et al., 2000). DLVO interaction potentials were calculated using the linear superpostion approximation for electrostatic potentials, and retarded Van der Waals interactions using a characteristic wavelength of 100 nm. Aggregation rates were calculated using the Fuchs approach assuming a minimal approach distance of 1 nm (Elimelech et al., 1995). Hamaker constants were taken from literature (Leong and Ong, 2003; Novich and Ring, 1984).



Figure 4. Electron microscopy images of nanoparticle heteroaggregation. a) Heteroaggregate of a silica particle with smaller iron hydroxide and clay particles and biological debris. The scale bar corresponds to 250 nm.(Buffle et al., 1998) b) TiO₂ nanoparticle aggregated at the edges of a kaolinite clay crystal. A single TiO₂ nanoparticle can be seen in the upper left corner (Tokarsky et al., 2012) c) TiO₂ ENM deposited on soil grains of an eutric cambisol (Nickel et al., 2012) and d) CeO₂ nanoparticle heteroaggregate from a spiked loamy soil suspension (Cornelis et al., 2011).



Figure 5. Literature Hamaker constants in water as a function of material density. The high scatter is caused by differing methods on how the constants were obtained.



Figure 6. The shift in PZC as a function of DOM concentration adsorbed on three different ENMs. ^aHA: Humic Acid; ^bSRFA: Suwannee River fulvic Acid (Data from (Domingos et al., 2009; Nickel et al., 2012; Thio et al., 2011; Yang et al., 2009).



Increasing DOM molecular weight, rigidity

Figure 7. Effects of DOM on enhancement or inhibition of ENM – ENM or ENM – colloid interactions.

TABLES

Table 1: Representative points of zero charge/iso-electric points ranges for uncoated, mineralogically pure naturally occurring colloids. Values from (Illes and Tombacz, 2006; Kosmulski, 2009; Stumm and Morgan, 1996; Tombacz and Szekeres, 2004; Tombacz and Szekeres, 2006)

Mineral	PZC/IEP	Mineral	PZC/IEP
SiO ₂	2 - 2.5	Goethite	7
Kaolinite (face/edge)	3.0 – 4.6 / 6.5	HFO	7.9 - 8.5
Montmorillonite (face/edge)	2.0 - 3.5 /6.5	Hematite	7.0 - 8.8
α -Al ₂ O ₃	8.3 – 9.4	Ferrihydrite	8.5
α -Al(OH) ₃	5	δ-MnO ₂	2.8
γ-ΑΙΟΟΗ	7.3 8.2	β-MnO ₂	7.2 - 8.7
albite	2.0	Feldspars	2.0 - 2.4

Table 2. Retention and/or transp	ort experiments	of ENM in natura	l soils.
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ENM	Test system	Main findings	Ref.
Ag - PVP coated -	batch retention of 16	ENM retention increased with granulometric	(Cornelis et
40 nm	soils.	clay content	al., 2012)
Ag – PVP coated -	saturated columns of 11	ENM retention higher in soils with high oxalate	(Cornelis et
40 nm	soils	extractable aluminium and low organic carbon	al., 2013)
Ag - citrate coated -	saturated columns of 3	ENM retention increased with granulometric	(Sagee et al.,
30 nm	mixtures of size	clay fraction, reduced with humic acid addition	2012)
	fractions of saturated	or pre-leaching of chloride.	
	soils and sand.		
Ag – uncoated/citrate	Mineral rich (TOC	Higher mobility of all types of silver in the	(Coutris et
coated 19 nm / 5 nm	14.9 g/kg) and organic	mineral soil type. The citrate coated Ag showed	al., 2012)
	rich (TOC 142 g/kg)	a higher mobility, but the bio-accessible fraction	
	unsaturated natural	of the uncoated Ag increased over time	
	agricultural soils		
Al $-$ uncoated $-$ 50,	saturated columns of a	ENM retention higher in loamy soil. Higher	(Darlington
80 and 120 nm.	loamy soil and sand.	retention for positively charged particles.	et al., 2009)
		Retention decreased upon phosphate addition.	
ZnO –	saturated columns of a	ENM retention higher in loamy soil and higher	(Zhao et al.,
uncoated/citrate	sandy and sandy-loamy	with increased salinity. Citrate coated ZnO	2012a)
coating - 10 nm	soil	higher mobility than uncoated ZnO.	
CdSe – polyacrilic	saturated homogenous	ENM retention higher in loamy sand and higher	(Quevedo
acid coated 5 nm -	sand and loamy sand	with increased salinity. Different coatings	and Tufenkji,
and CdTe –		interacted differently with soil components in	2012)
octadecylamine		the loamy sand.	
coated - 9 nm			
nC ₆₀ - uncoated	saturated columns of a	ENM retention higher in sandy soil and higher	(Zhang et al.,
	sandy soil and sand	with increased salinity.	2012)
nC ₆₀ - uncoated	saturated columns of	ENM retention increased with granulometric	(Wang et al.,
	two soils.	clay and organic matter content, decreased upon	2010)
		addition of dissolved humic acids.	
CNT – carboxyl	saturated column of a	ENM retention increased with salinity. High	(Jaisi and
functionalised	sandy loam soil	straining because of large aspect ratio.	Elimelech,
			2009)
TiO ₂ and Sb ₂ O ₃	Natural floodplain soil	Negatively charged ENM showed higher	(Duester et
		transport. Transport with the pore water.	al., 2011)
TiO ₂ uncoated and	saturated columns of	Positively charged ENM showed high retention	(Kuhlbusch
coated	three natural soil types	unless coated. Only single agglomerates were	et al., 2012)
		transported. Higher transport was observed for	
		the coated material. No clear correlation	
		between clay or pH and the mobility of the	

		ENMs	
TiO ₂	saturated columns of	Positively charged ENM showed high retention,	(Nickel et al.,
	three natural soil types	Only single agglomerates were transported.	2012)
TiO ₂ – uncoated –	saturated columns of 12	ENM retention increased with granulometric	(Fang et al.,
35 nm	stacked saturated soils.	clay contents and salinity	2009)
CeO ₂ – uncoated -	batch retention of 16	ENM retention increased with granulometric	(Cornelis et
130 nm aggregates	soils.	clay content, decreased with dissolved	al., 2011)
		phosphate concentration	

ENM	Surface modification	Test system	DOM type	Main findings	Reference
Ag	Unmodified, coated NP with PVP ^a or GA ^b	Spherical glass beads	PVP and GA	A high concentration of DOM leads to decreased deposition due to steric stabilisation if both the particle surface as well as the silica surface were covered with NOM. Lower concentration can lead to bridging.	(Lin and Wiesner, 2012)
Ag	Unmodified, citrate coated	Two loamy soils with high or low organic carbon content	Naturally occurring	All types of Ag ENM were more mobile in the soil with low DOM content.	(Coutris et al., 2012)
Ag	coated with PVP	Saturated columns of 11 natural soils	Naturally occurring	Weak negative correlation between Ag ENM collision efficiency and total carbon of soils	(Cornelis et al., 2013)
Cu	Undmodified	Saturated sand columns	SRHA or SRFA	Addition of DOM increased the mobility of Cu ENM but DOM concentrations > 1 mg L^{-1} do not further increase ENM transport.	(Jones and Su, 2012)
C ₆₀	Unmodified	QCM ^c coated with silica, unmodified or coated with SRHA	SRHA ^d	Addition of SRHA to unmodified silica increased the mobility of C_{60} . Addition of SRHA to precoated silica increased the mobility of C_{60} but only in the presence of NaCl, not in the presence of CaCl ₂ .	(Chen and Elimelech, 2008)
C ₆₀	Unmodified	Two natural soil types with high or low organic content	SRHA	Addition of SRHA increased the mobility of C ₆₀	(Wang et al., 2010)
C ₆₀ , MWCNT; SWCNT	Unmodified or C ₆₀ (OH) ₂₄	Spherical glass beads	SRHA	Addition of SRHA increased the mobility of C_{60} , whereas a mixture of SRHA and electrolytes increased settling and adsorption, divalent ions are more efficient than monovalent ions.	(Chae et al., 2012)
$\begin{array}{c} \text{TiO}_{2,} \\ \text{Fe}_{3}\text{O}_{4} \\ \text{CuO, ZnO} \end{array}$	Unmodified,	Spherical glass beads	Aldrich HA	Addition of DOM increased the mobility of all ENM. The strongest effect was observed for ZnO ENM.	(Ben-Moshe et al., 2010)
TiO ₂	Unmodified,	Saturated columns of 12 natural soils	Naturally occurring	TiO ₂ ENM stabilization in pore waters by DOM also increased the transport in saturated natural soil columns.	(Fang et al., 2009)
TiO ₂	TiO ₂ with NOM and E.coli	Saturated sand columns	SRHA	Addition of SRHA increased the transport the mobility of TiO ₂ ENM	(Chowdhury et al., 2012)
TiO ₂	Unmodified	QCM coated with silica	SRHA	Addition of SRHA decreased deposition	(Thio et al., 2011)
TiO ₂	Unmodified	Saturated sand columns	SRHA	Addition of SRHA increased the mobility of (positively charged) TiO_2 ENM and increased with higher SRHA concentrations at pH 5.7. Only a limited effect was observed at pH 9 where unmodified TiO_2 is also negatively charged.	(Chen et al., 2012b)

Table 3. Effect of dissolved organic matter on the fate and behaviour of different ENMs in (reference) soil columns

TiO ₂	Two	Unsaturated	Naturally	Low mobility of unmodified, positively charged ENM in the soil type with higher	(Kuhlbusch
	unmodified and	natural soil, with	occurring	organic content. For the coated material a higher mobility was observed, increasing	et al., 2012)
	one	high and low		with increasing organic content.	
	hydrophobic	organic carbon			
	TiO ₂	content			

^a PVP: Polyvinylpyrollidone ^b GA: Gum Arabic ^c QCM: Quartz crystal Microbalance ^d SRHA: Suwannee River Humic acid

		Intestine of	Excreted gut mucus of
	Intestine of isopod	earthworm	earthworms
Redox	Oxic	Anoxic	n.a.
pН	5.5-6.5	6.9	7.3
		$100 \text{ mg g}^{-1} \text{ dry}$	
Organic carbon	n.a.	weight	$6.5-24 \text{ mg L}^{-1}$
	(Zimmer and		
Reference	Brune, 2005)	(Horn et al., 2003)	(Sizmur et al., 2011)

Table 4. Chemical environment in intestines of soil organisms

Table 5. Concentrations of low	molecular o	organic cor	mpounds in	soil solution	rhizospheres
released by plants					

				Concentration	
Species	Medium	Setup	Compound	$(\mu mol L^{-1})$	Reference
					(Mimmo et
Lupinus alba	Soil eluate	Mesocosm	Citrate	161	al., 2011)
-					(Mimmo et
Lupinus alba	Soil eluate	Mesocosm	Oxalate	909	al., 2011)
-					(Mimmo et
Brassica napus	Soil eluate	Mesocosm	Citrate	4.7	al., 2011)
-					(Mimmo et
Brassica napus	Soil eluate	Mesocosm	Oxalate	329	al., 2011)
-					(van Hees
- Pinus sylvestris					et al.,
- Picea abies	Soil solution	Field sites Sweden	Citrate	66 - 116	2005)
					(van Hees
- Pinus sylvestris					et al.,
- Picea abies	Soil solution	Field sites Sweden	Oxalate	1.7 - 5.8	2005)

APPENDIX.

	ENM or		-	Type of		
	aggregate size	Plant		exposure		
ENM	(nm)	species	Main findings	medium	Reference	Remarks
		Triticum	MWCNTs punctured		(Wild and	
MWCNT	110 - 9000	aestivum	walls of roots	Hydroponic	Jones, 2009)	
		Triticum	Aggregation at root		(Wild and	
TiO	< 100	aestivum	surface	Hydroponic	Jones, 2009)	No uptake confirmed
		Triticum	Aggregation at root		(Wild and	
CeO2	< 20	aestivum	surface	Hydroponic	Jones, 2009)	No uptake confirmed
			Aggregation at root			
CdSe/ZnS		Arabidopsis	surface, uptake of QDs in		(Navarro et	
QDs	6-12	thaliana	roots	Hydroponic	al., 2012)	No uptake confirmed
						Glycine conjugated QDs showed highest
			Uptake of QDs only			uptake: in vacuoles of the fungi hyphae
			when conjugated with			and in vascular tissues of the root cells.
Carboxylated			amino group of glycine	1:1 sand :	(Whiteside	Chitosan conjugated QDs were observed in
Cd/Se QDs		Poa annua	or chitosan	vermiculite	et al., 2009)	the hyphae, but not in the root cells
			Uptake of C/0 by			
			osmotic pressure through			
		D.	pores in cell walls, by	TT 1 ·		
070		Rice	intercellular	Hydroponic	(T	
C/U	1 10	(Oryza	plasmadesmata or by	on tissue	(Lin et al., 2000)	
Iunerene	1.19	sanva)	symplastic uptake	paper	2009)	
		O	Minimal untaka of	Hydropoliic on tissue	(Lin at al	
MWCNT	240(d)	Oryza		on ussue	(LIII et al., 2000)	
	$240(a_{h})$	suuvu	NDs wara raadilyt takan	paper	2009)	
			up although route of		(7 hu et al	
			up, annough foure of		(2.10 Ct al., 2008)	Size as from manufacturer DIS showed
Fe3O4		Cucurbita	much aggregation at root		(Wang et al	larger sizes (20-2000nm) no translocation
nanonarticle	20	maxima	surface	Hydroponic	(0.011)	to other parts of pants detected
nanoparticie	20	талта	Aggregations of NPs at	itydiopolite	20110)	to other parts of parts detected
			roots some but verv			
		Lolium	limited uptake of ZnO-		(Lin and	
ZnO	20	perenne	NPs in apoplast and	Hydroponic	Xing, 2008)	Uptake of Zn+ occurred.

*Table A1. Studies investigating ENM by plant uptake.

			protoplast of the root endodermis.\ Root uptake not assessed, no translocation of Ce to other parts of plants		(Birhaum et	No root tissues analysed, so untake in roots
CeO2	37	Zea mays - Lolium	detectable	Soil	(Diroddin et al., 2010)	can not be ruled out.
CdSe/ZnS		- Allium	No uptake of QDs by the		(Al-Salim et	QDs were glycine-, mercaptosuccinic acid-
QDs	6.5	cepa	roots	Hydroponic	al., 2011)	, cysteine- and cysteamine-conjugated QDs Au was accumulated as particle, which was confirmed by analyses of particles of consumer of tobacco. Zeta potential
		Nicotiana	Uptake of Au was		(Judy et al.,	appeared more important in driving uptake
Au	5, 10, 15	tabacum	confirmed in plant tissue	Hydroponic	2011)	than size. SWNT were non-functionalised and functionalised with poly 2
			at root surface. no uptake		(Canas et al.,	aminobenzenesulfonic acid. Detection
SWCNT	8 x > 100	various	was visible CuO, ZnO and Cu ENM	Hydroponic	2008)	performed with SEM
		Cucumis	accumulate in			
CuO, Cu, ZnO, Zn	50	sativus	endodermys roots, Zn	Undrononia	(Kim et al., 2012b)	Detection with TEM
ZIIO, ZII	50			Trydropollic	20120)	Cu NPs cross the cell membrane and
		- Phaseolus				homoagglomorates and
		raiatus - Triticum	Untake of Cu ENM		(Lee et al	with the cells. Accumulation of FNM
Cu	ca. 30	aestivum	visualised by TEM	Agar	2008)	dose dependent.
Sucrose			Untake of sucrose coated			Anatase TiO_2 no untake of ENM in seeds
with Alizarin		Arabidopsis	TiO ₂ shown in tips of		(Kurepa et	by protection of mucilage. Seedlings 5 day
red labeling	2.8	thaliana	roots	Hydroponic	al., 2010)	old
CeO2 hare			Uptake of particles			Coated ENM more accumulated in
and alginate			properties and particle		(Zhao et al.,	in non-enriched soil. Uptake via apoplastic
coated	8 (primary)	Zea mays	coating	Soil	2012b)	pathway
			Uptake of ENM and		(Theo at al	Uptake of ZnO ENM and aggregates via
ZnO	$389(d_h)$	Zea mays	cofirmed.	Soil	(Zhao et al., 2012c)	transport through endordermis via

		- Oryza sativa				symplastic pathway. No upper limit of aggregation size provided
		- Cucurhita				
Au, coated		maxima	Uptale of negatively			
with		- Raphanus	charged ENM was higher			
differently		Sativa	than positively charged			Accumulation to shoots was higher for
charged		- Lolium	Au-ENM. Species		(Zhu et al.,	positively charged ENM, but did not occur
ligands	6	perenne	differed in uptake	Hydroponic	2012)	in radish amd pumpkin