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Original

Human health risk assessment for nanoparticle-contaminated aquifer systems / Tosco, T.; Sethi, R.. - In: ENVIRONMENTAL POLLUTION. - ISSN 0269-7491. - 239:(2018), pp. 242-252. [10.1016/j.envpol.2018.03.041]

Availability:

This version is available at: 11583/2784354 since: 2020-01-23T10:53:10Z

Publisher:

Elsevier Ltd

Published

DOI:10.1016/j.envpol.2018.03.041

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Human health risk assessment for aquifer systems at nanoparticle-contaminated sites

Submitted to

Environmental Pollution

Revised manuscript - March 2018

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Abstract

31

32 Nanosized particles (NPs), such as TiO₂, Silver, graphene NPs, nanoscale zero-valent iron, carbon
33 nanotubes, etc., are increasingly used in industrial processes, and releases at production plants and
34 from landfills are likely scenarios for the next years. As a consequence, appropriate procedures and
35 tools to quantify the risks for human health associated to these releases are needed.

36 The tiered approach of the standard ASTM procedure (ASTM-E2081-00) is today the most applied
37 for human health risk assessment at sites contaminated by chemical substances, but it cannot be
38 directly applied to nanoparticles: NP transport along migration pathways follows mechanisms
39 significantly different from those of chemicals; moreover, and also toxicity indicators (namely,
40 reference dose and slope factor) are NP-specific. In this work a risk assessment approach modified
41 for NPs is proposed, with a specific application at Tier 2 to migration in groundwater. The standard
42 ASTM equations are modified to include NP-specific transport mechanisms. NPs in natural
43 environments are typically characterized by a heterogeneous set of NPs having different size, shape,
44 coating, etc. (all properties having a significant impact on both mobility and toxicity). To take into
45 account this heterogeneity, the proposed approach divides the NP population into classes, each
46 having specific transport and toxicity properties, and simulates them as independent species. The
47 approach is finally applied to a test case simulating the release of heterogeneous Silver NPs from a
48 landfill. The results show that taking into account the size-dependent mobility of the particles
49 provides a more accurate result compared to the direct application of the standard ASTM procedure.
50 In particular, the latter tends to underestimate the overall toxic risk associated to the nP release.

51

Capsule

52

53 A risk assessment procedure for nanoparticle releases at contaminated sites is proposed. The
54 standard human health risk assessment models for subsurface migration are adapted to nanoparticles

55

57 **1. Introduction**

58 The use of engineered nanoparticles (NPs) in industrial applications and commercial products have
59 grown substantially in recent years. However, despite their great potential for technology, NPs can
60 also represent a significant, and still largely unknown, environmental hazard. NP-containing
61 products are already widely available on the market, or expected to be in few years, likely leading
62 to the dissemination of large amounts of NPs in the environment. Despite the advanced stage of the
63 research on their technological applications, the possible impacts of NPs on the environment are
64 less studied, which may pose concerns on safety as well as social acceptance of NP-based products.

65 In recent years, a growing body of studies have been devoted to the assessment of potential risks
66 associated to the release of NPs, including the identification of preferential migration pathways, the
67 estimation of NP concentration in the different environmental compartments, and the assessment of
68 their toxicity toward human and ecological targets (Hendren et al., 2013; Garner and Keller, 2014).
69 The majority of these studies focus on the fate of NPs gradually released from diffuse sources, eg.
70 use of NPs-containing fertilizers and sludge in agriculture, direct release from consumer products
71 (eg. paints, textiles, fuels, etc.), and incomplete removal of NPs in wastewater treatment plants
72 (Gottschalk et al., 2009; Batley et al., 2013; Kaegi et al., 2013; Klitzke et al., 2015). A quantitative
73 estimation of potential environmental concentrations of representative NPs from diffuse sources,
74 and the associated toxicity risks, was proposed by several authors. However, comprehensive studies
75 including several NPs and release scenarios are fewer, also due to the extreme complexity of the
76 topic, eg. (Boxall et al., 2007; Hendren et al., 2013; Sun et al., 2014; Dale et al., 2015). The release
77 from diffuse sources is relevant in terms of total mass and accumulation in the environment, but, at
78 the moment, the resulting average NP environmental concentrations are modest, and far below
79 toxicity limits (Batley et al., 2013; Garner and Keller, 2014). Conversely, releases from point
80 sources can result in significantly higher concentrations (and consequently, higher potential risks) at
81 a local scale. Typical release scenarios include leaching from landfills where NPs-containing
82 products are disposed; releases at industrial sites where NPs are manufactured, due to continuous,
83 unintentional losses during normal activities of the plant, or following major accidents which result
84 in the release and consequent accumulation of NPs in the soil and subsoil; long-term re-
85 mobilization of NPs delivered on purpose at contaminated sites for groundwater remediation.

86 The possible fate of significant amounts of engineered NPs released at point sources, and the
87 associated risk posed to human health, have been scarcely faced by researchers at the moment. To
88 this aim, long-term (chronic) effects could be quantified and evaluated using risk assessment
89 procedures, similar to those conventionally employed in the management of sites contaminated by
90 chemical compounds. The most widely used approach in this sense is the Risk-Based Corrective
91 Action (RBCA) ASTM standard, which quantifies the toxic and carcinogenic risk arising for human
92 receptors due to the exposure to the chemical substances released at contaminated sites (ASTM,
93 2015). Risk assessment approaches, procedures and computational tools are available and largely
94 used for chemical substances. Extended and modified formulations of the analytical equations of the
95 standard ASTM approach have been recently proposed to incorporate further processes (eg.
96 biodegradation in the unsaturated zone) and tools (eg. sensitivity analysis) (Avagliano et al., 2005;
97 Lemke and Bahrou, 2009; Baciocchi et al., 2010; Verginelli and Baciocchi, 2013). The short- and
98 intermediate-term fate and toxicity of NPs released in major accidents has been recently faced by
99 Nowack et al. (2014) as well as risks associated to the use of NPs as pesticides (Kookana et al.,
100 2014). However, approaches and tools for the estimation of the risk associated to sites contaminated
101 by NPs are almost lacking at the moment: few works were proposed to extend fate models of
102 current risk assessment procedures to nanomaterials (Dale et al., 2014; Praetorius et al., 2014), and
103 a comprehensive approach for the assessment of long-term risks is still missing.

104 Several challenges are to be faced for a successful adaptation of the ASTM procedure to NPs: on
105 the one hand, particle-specific toxicity parameters (eg. Chronic Reference Dose RfD and Slope
106 Factor SF), requested in the procedure, have been already determined for very few particles; on the
107 other hand, the processes controlling NP migration in the environmental compartments may be
108 significantly different from those associated to chemical substances. Moreover, both mobility and
109 toxicity depend not only on the NP composition, but also on their size, shape, eventual coating, and
110 environmental modifications which particles may undergo after release (eg. oxidation, dissolution,
111 interaction with organic matter, etc.). In particular, a key property which poses major challenges in
112 the adaptation of the ASTM transport models to NPs is particle heterogeneity. Even NPs which are
113 fairly homogeneous when released may significantly change their properties over time, and result in
114 a very heterogeneous population on the long term (Westerhoff and Nowack, 2012). Nanoparticles
115 may be heterogeneous in size, shape, surface coating etc., which are all properties with a significant
116 effect on the NP overall mobility in the subsurface. Among these properties, particle size is
117 definitely a dominant one (Tufenkji and Elimelech, 2004). Particles having the same composition
118 and shape, but different size, are characterized by a different mobility in groundwater.

119 The toxic effects of nanoparticles have been extensively investigated in recent years, both in vivo
120 and in vitro, but very few toxicity indicators have been determined (Schilling et al., 2010; Shi et al.,
121 2013). Sets of RfD and SF values for particles having the same composition but different size, or
122 coating, are not available in the literature. Moreover, no standard classification of NPs as
123 carcinogenic is available. Ecotoxicity have been quantitatively assessed in some cases for selected
124 nanoparticles (eg. Ag, TiO₂, fullerene, carbon nanotubes), while toxicity limits relevant to human
125 risk assessment have not been standardized yet (Demir et al., 2013; Johnston et al., 2013; Comfort
126 et al., 2014; Siripattanakul-Ratpukdi and Fürhacker, 2014). Values of RfD for Ag NPs have been
127 proposed (Kim et al., 2010; Windler et al., 2013), while in other cases the use of the RfD of the
128 corresponding bulk substances is recommended (Varner et al., 2010).

129 In this work, the framework for the development of risk assessment procedures for NPs-
130 contaminated sites is presented, discussing the modifications to the standard procedures and
131 mathematical tools already available for chemicals, and the main challenges still to be faced for the
132 application of such a procedure to real contaminated sites. In particular, the crucial role of particle
133 size is discussed, and an adaptation of the standard ASTM procedure at Tier 2 is proposed for NP
134 releases. NP-specific transport models are simplified and adapted to the analytical solutions in the
135 standard ASTM approach, and the selection of appropriate toxicity indicators is briefly discussed.
136 An example of risk assessment for a NP-contaminated site is finally presented.

137

138 **2. Development of a risk assessment procedure adapted to** 139 **NPs**

140 The ASTM procedure follows a tiered approach, with complexity increasing from Tier 1 to Tier 3.
141 Tier 1, based on a direct comparison of observed concentrations against screening levels reported in
142 look-up tables, is not site-specific, and is scarcely applied, apart from extremely simplified
143 scenarios. In most cases, a site-specific procedure is adopted, based on the use of analytical or
144 numerical solutions (Tier 2 or 3, respectively) to describe the migration of the contaminants from
145 the source to the potential receptors through different migration pathways. Despite Tier 3 allows for
146 the application of more realistic fate and transport models, Tier 2 is more commonly applied due to
147 the simplicity of use and collectability of the site-specific data required for its application.

148 Following the ASTM standard (ASTM, 2015), a risk analysis at Tier 2 and 3 is composed by three
149 stages:

- 150 – Stage 1, including the identification of the release source and of the relevant migration
151 pathways in the environmental matrices, from the source to the point of exposition (POE)
152 where potential receptors are located.
- 153 – Stage 2, including predictive simulation of contaminant spreading along the migration
154 pathways previously identified. Analytical (Tier 2) or numerical (Tier 3) models are applied
155 to quantify the expected concentration at POE (C_{POE}), provided that the concentration at the
156 source (C_0) is known;
- 157 – Stage 3, the estimation of the impact on potential receptors in terms of chronic toxicity and
158 carcinogenic effects.

159 In the next paragraphs, for each stage, the adaptations to extend the ASTM approach to NP-
160 contaminated sites are discussed.

161

162 ***2.1 Stage 1: Major migration pathways for NP release***

163 The ASTM approach is typically applied to contaminated sites. In this case, three major exposure
164 pathways are identified, namely exposure to contaminated soil, contaminated air, and contaminated
165 groundwater. The first is associated to a direct contact of the potential receptor with the
166 contaminated soil; it is therefore limited to on-site exposure, and the definition of migration models
167 is not necessary. Since for most NPs a relatively fast precipitation onto the soil is expected (Garner
168 and Keller, 2014), also migration through air is likely relevant only for on-site exposure.

169 The subsoil very often represents the most likely migration scenario for the long-term NP fate.
170 Consequently, in this work we focus on this scenario, and NP migration through the air will not be
171 discussed. However, it is worth to mention that, under specific scenarios which may lead to NP
172 dispersion in the air, adequate transport models should be developed and discussed following an
173 approach similar to the one applied here for the subsurface.

174

175 ***2.2 Stage 2: Migration of the NPs from the source to the potential*** 176 ***receptors***

177 Particle transport in groundwater is controlled by mechanisms which can only be partially
178 assimilated to those controlling the migration of chemical substances. In the standard ASTM

179 procedure the migration of a contaminant from the source to the point of exposition of the potential
180 receptor is schematized through the following steps (Figure 1):

- 181 – in the source area, the contaminant is dissolved from solid phase into pore water (from S_{soil}
182 to C_{leach}); the process is quantified by the Soil-Water Partition Factor ($K_{sw} = S_{soil}/C_{leach}$). In
183 case of thick unsaturated zone and/or easily degradable contaminants, additional mitigation
184 processes can be included and modeled at this stage, thus leading to a reduced concentration
185 in the leachate while reaching groundwater (Connor et al., 2007; Verginelli and Baciocchi,
186 2013).
- 187 – When reaching the water table, the leachate mixes with groundwater (from C_{leach} to C_0); the
188 process is quantified by the Leachate Dilution Factor ($LDF = C_{leach}/C_0$).
- 189 – The contaminant migrates through the aquifer toward the potential receptor (from C_0 to
190 C_{POE}); the process is represented by the Dilution Attenuation Factor ($DAF = C_0/C_{POE}$).

191 The first two steps may be included in the so-called Leaching Factor $LF = 1/(K_{sw} \cdot LDF)$.

192 The overall attenuation from the source to the potential receptor is represented by the Natural
193 Attenuation Factor $NAF [L^3M^{-1}]$:

$$194 \quad NAF = \frac{S_{soil}}{C_{POE}} = K_{sw} \cdot LDF \cdot DAF \quad (1)$$

195 where S_{soil} is the contaminant concentration in solid phase at the source, expressed as mass of
196 contaminant per unit mass of soil [MM^{-1}], and C_{POE} is the contaminant concentration in water at
197 POE [ML^{-3}].

198 At Tier 2, simplified scenarios for contaminant dissolution and transport are adopted, and analytical
199 transport models are applied to predict the concentrations at the potential receptors (C_{POE}). A
200 summary of Tier 2 analytical solutions is reported in Supporting Information. At Tier 3, more
201 complex scenarios can be considered, and numerical solutions are adopted to simulate the migration
202 of the contaminants (Baciocchi et al., 2010; Pinedo et al., 2014; ASTM, 2015).

203 To take into account the influence of NP heterogeneity (eg. NPs heterogeneous in size) the particle
204 population can be divided into classes, and the transport of each class modeled independently. As a
205 consequence, one value of NAF is to be calculated per each class i , NAF_i :

$$206 \quad NAF_i = \frac{S_{soil,i}}{C_{POE,i}} = K_{sw,i} \cdot LDF_i \cdot DAF_i \quad (2)$$

207 Being particle transport class-dependent rather than mass-dependent, it is more convenient to
 208 consider number concentrations rather than mass concentrations, thus

$$209 \quad C_i = m_i N_{w,i} \quad \text{and} \quad C = \sum_i m_i N_{w,i} \quad (3a)$$

$$210 \quad S_i = \frac{1-\varepsilon}{\rho_s} m_i N_{s,i} \quad \text{and} \quad S = \frac{1-\varepsilon}{\rho_s} \sum_i m_i N_{s,i} \quad (3b)$$

211 where $N_{w,i}$ and $N_{s,i}$ are the number concentration of particles of the i -th class per unit volume of
 212 water and of solid phase, respectively [L^{-3}], m_i is the mass of a particle of the i -th class [M], ρ_s is the
 213 solid matrix bulk density [ML^{-3}], ε is the porosity [-]. The overall mass concentrations for NPs in
 214 liquid and solid phase, C and S , can be obtained summing up mass concentrations of the individual
 215 classes, C_i and S_i .

216 Therefore, NAF_i can be defined as

$$217 \quad NAF_i = \frac{1-\varepsilon}{\rho_s} \frac{N_{s,soil,i}}{N_{w,POE,i}} \quad (4)$$

218 Similar definitions can be written for $K_{sw,i}$, LDF_i and DAF_i (Supporting Information).

219

220

221 **2.2.1 Definition of DAF for nanoparticles**

222 In the standard ASTM procedure, the spreading of chemical substances in groundwater (and
 223 consequently NAF) is quantified by analytical or numerical models describing the contaminant
 224 transport due to advection, dispersion, sorption onto the solid matrix, degradation, and
 225 volatilization. Assuming first order degradation/volatilization and linear equilibrium sorption, the
 226 partial differential equation (PDE) describing the solute transport in groundwater is:

$$227 \quad \frac{\partial}{\partial t}(\varepsilon RC) + \nabla \cdot (uC) - \nabla \cdot (\varepsilon D \nabla C) + \varepsilon \lambda C = 0 \quad (5)$$

228 where u is the specific discharge rate [LT^{-1}], D is the hydrodynamic dispersion tensor [L^2T^{-1}], λ is
 229 the first order degradation rate constant (describing either chemical degradation, biodegradation or
 230 volatilization) [T^{-1}], and R is the retardation factor (describing linear equilibrium sorption onto the
 231 porous matrix). At Tier 2, the ASTM procedure suggests the use of the analytical solution of

232 Domenico (Domenico, 1987) for the calculation of C_{POE} . In particular, the solution at steady state is
 233 usually adopted:

$$234 \quad \frac{C_{POE}}{C_0} = \frac{1}{4} \exp\left[\left(\frac{x}{2\alpha_x}\right)\left(1 - \sqrt{1 + \frac{4\lambda\alpha_x}{v}}\right)\right] \cdot \left[\operatorname{erf}\left(\frac{y + \frac{L_w}{2}}{2\sqrt{\alpha_y x}}\right) - \operatorname{erf}\left(\frac{y - \frac{L_w}{2}}{2\sqrt{\alpha_y x}}\right) \right] \cdot \left[\operatorname{erf}\left(\frac{z + \delta_{sw}}{2\sqrt{\alpha_z x}}\right) - \operatorname{erf}\left(\frac{z - \delta_{sw}}{2\sqrt{\alpha_z x}}\right) \right] \quad (6)$$

235 where v is the seepage velocity u/ε [LT^{-1}], L_w and δ_{sw} are the transversal and vertical extents of the
 236 contamination source (Figure 1) [L], α_x , α_y and α_z are the horizontal, transversal and vertical
 237 dispersivities [L]. The Domenico transient solution is reported in the Supporting Information.

238 Two major points can be identified which make the direct application of Eq. 5 (and its analytical or
 239 numerical solutions) inappropriate to NPs as it is. These two aspects are the influence of
 240 heterogeneities within the NP population (above all, the heterogeneity in size), and the intrinsic
 241 difference of the mechanisms controlling the NP interactions with the porous medium, compared to
 242 solutes. The first aspect can be taken into account by dividing the NP population into classes, with
 243 different transport properties, and consequently calculating NAF_i per each class, as defined in Eq. 2.
 244 Concerning the second aspect, NP fate in the subsoil follows mechanisms noticeably different from
 245 those typical of solutes. Particle transport is controlled by advection, dispersion and kinetic mass
 246 transfer between liquid and solid phase (attachment/detachment) (Kretzschmar et al., 1999; Tosco et
 247 al., 2009). Mechanical filtration of large particles or aggregates may also play a relevant role. In
 248 unsaturated soils, particle attachment at the air-water interface can also have a significant impact
 249 (Sim and Chrysikopoulos, 1999; Bradford and Torkzaban, 2008). A vast literature is available on
 250 the different processes and the corresponding mathematical formulations (Johnson et al., 1996;
 251 Bradford et al., 2002; Johnson et al., 2007; Petosa et al., 2010; Messina et al., 2015), and a review
 252 of the topic is beyond the purpose of this paper.

253 Considering the transport mechanisms led by Eq. 5, some are clearly inapplicable to NPs, eg. the
 254 contaminant volatilization. Also NP biodegradation is unlikely: bacteria-mediated transformations
 255 are expected for most NPs, but their effect is a modification of surface properties and transport
 256 behavior, rather than a "disappearance" of the particles (Lowry et al., 2012; Nowack et al., 2012;
 257 Schaumann et al., 2015). Moreover, the equilibrium sorption of a solute can only be partly
 258 assimilated to the kinetic deposition and release of NPs, as widely debated in the recent literature
 259 (Dale et al., 2014; Praetorius et al., 2014; Cornelis, 2015). As a consequence, the transport models
 260 adopted in the standard ASTM procedure cannot be directly applied to simulate the transport of

261 NPs, but must be adapted and extended to include NP-relevant mechanisms of transport. Neglecting
 262 NP aggregation and/or breakage of aggregates, the model equation for the i -th class of NPs is

$$263 \quad \frac{\partial}{\partial t}(\varepsilon N_{w,i}) + \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,i}] + \nabla \cdot (uN_{w,i}) - \nabla \cdot (\varepsilon D \nabla N_{w,i}) = 0 \quad (7)$$

264 The second term of Eq. 7 represents the interactions of the suspended NPs with the porous matrix,
 265 and can be expressed, in a general form, as

$$266 \quad \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,i}] = \varepsilon k_{a,i} \psi_i N_{w,i} - k_{d,i} (1-\varepsilon)N_{s,i} \quad (8)$$

267 where $k_{a,i}$ and $k_{d,i}$ are respectively the attachment and detachment rates [T^{-1}] of the i -th class, and ψ_i
 268 is a kinetic function depending on the specific attachment mechanism (linear deposition, blocking,
 269 ripening, straining...). The three parameters all depend on particle size.

270 An analytical solution to Eqs. 7-8 for 3D domains, equivalent to the Domenico's solution, is not
 271 available. Analytical solutions were developed for 1D domains (Šimůnek et al., 2008) and for
 272 simplified 3D (Sim and Chrysikopoulos, 1998), but for general 3D domains numerical solutions are
 273 requested, eg. MNM3D (Bianco et al., 2016). Even if such models can provide an accurate and
 274 physically meaningful description of particle transport processes, they are too complex for a direct
 275 application at Tier 2. For this reason, we propose here an adaptation of Domenico's analytical
 276 solution to solve Eqs. 7-8, for each class of NPs i , to simulate NP transport in 3D scenarios suitable
 277 for a Tier 2 risk analysis.

278 To this aim, Eqs. 7-8 must be first re-arranged to the structure of Eq. 5 (Table 1). For example,
 279 comparing Eqs. 7-8 to Eq. 5, it can be observed that linear irreversible attachment ($\psi_i=1$, $k_{d,i}=0$ in
 280 Eq. 8) can be formally simulated as a first order degradation without any simplifying assumption.
 281 Conversely, NP deposition/release can be approximated as a sorption process only for those
 282 formulations leading to a dynamic equilibrium between solid and liquid phase (eg. blocking, linear
 283 reversible deposition), and only under specific simplifying assumptions.

284 From a formal point of view, a dynamic equilibrium is possible when Eq. 7 can be re-arranged in
 285 the form of an implicit kinetic formulation (Azizian, 2004):

$$286 \quad \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,i}] = K_{eq,i} (N_{s,i}^* - N_{s,i}) \quad (9)$$

287 where $N_{s,i}^*$ [-] is the NP concentration in the solid phase when the dynamic balance is reached, and
288 $K_{eq,i}$ [$ML^{-3}T^{-1}$] is the implicit rate constant. Both $N_{s,i}^*$ and $K_{eq,i}$ depend on the considered
289 deposition/release mechanism.

290 If Eq. 9 can be written, a retardation factor can be formally defined as:

$$291 \quad R_i = 1 + \frac{1 - \varepsilon}{\varepsilon} \frac{N_{s,i}^*}{N_w} \quad (10)$$

292 The approximation of dynamic equilibrium, and therefore the applicability of a retardation factor, is
293 valid when the characteristic time of the attachment/detachment process is significantly lower than
294 the characteristic time of advection. Similarly to solute sorption (Azizian, 2004; Werner et al.,
295 2012), also for NPs it is possible to evaluate how far conditions are from equilibrium by means of
296 the Damköler number:

$$297 \quad Da_i = \frac{K_{eq,i} L}{u} \quad (11)$$

298 where L is the scale of the problem (here, the x coordinate). Kinetic processes can be neglected for
299 $Da > 1$.

300 From a practical point of view, equilibrium is established and NP deposition can be approximated
301 by a retardation factor when $Da > 1$, that is for $L > u / ((1 - \varepsilon) k_{d2})$.

302 If a particle size distribution is considered, R_i is to be defined per each class. A summary of the
303 values of λ_i and R_i for the most common deposition kinetics is provided in Table 1. Details on the
304 applicability of this approximation, and a step-by-step procedure for the selection of the appropriate
305 approximation are provided in the Supporting Information.

306 In conclusion, it is strongly recommended that, when developing a comprehensive NP risk
307 assessment tool (likely, at Tier 3), the impact of a heterogeneous NP population is included in the
308 transport and fate models, namely using solutions to Eqs. 7-8 for a heterogeneous NP population
309 with class-dependent parameters, rather than using a homogeneous one. Nevertheless, for a first
310 screening, at Tier 2 simplifying assumptions can be made concerning NP transport on the long term
311 and over large scales, and consequently the mathematical formulation adopted in standard ASTM at
312 Tier 2 (i.e. using Eq. 6) can be adopted also for NPs without major modifications (see Paragraph 3).

313

314 **2.3 Stage 3: risk estimate**

315 The standard ASTM procedure quantifies the risk associated to the chronic exposure to a
316 contaminant or, as in this case, to nanoparticles, through two indexes, namely the Hazard Quotient
317 (HQ) for toxic effects, and the Incremental Lifetime Cancer Risk (ILCR) for carcinogenic effects.
318 The two indexes cumulate the chronic effects generated by the different exposure pathways and
319 substances (ASTM, 2015).

320 For a single substance and for the exposure due to injection of groundwater, the HQ index is
321 calculated as the ratio of the average intake of substance at POE, and the Reference Dose:

$$322 \quad HQ = \frac{C_{POE} \cdot E}{RfD} \quad (12)$$

323 where E is the exposure rate (i.e. average amount of water ingested per day per unit body weight)
324 [$L^3M^{-1}T^{-1}$] and RfD is the Reference Dose [$L^3M^{-1}T^{-1}$], that is the maximum dose below which no
325 chronic toxic effect is observed (Connor et al., 2007; ASTM, 2015). RfD values are typically
326 defined from NOAEL (Not Observed Adverse Effect Level) or LOAEL (Lowest Observed Adverse
327 Effects Level), and standardized in databases, eg. RAIS (<http://rais.ornl.gov/tutorials/toxvals.html>).
328 $HQ < 1$ corresponds to an acceptable toxic risk, $HQ > 1$ to an unacceptable toxic risk.

329 For carcinogenic effects, the ILCR index is calculated as the product of the average intake $C_{POE} \cdot E$
330 and the Slope Factor SF [-], determined from dose-response curves:

$$331 \quad ILCR = C_{POE} \cdot E \cdot SF \quad (13)$$

332 Figure 2 reports a comparison of different scenarios for the calculation of the toxic effects of NPs,
333 assuming different approximations. Scenario A corresponds to the standard ASTM procedure for
334 chemical substances: transport models describe how the NP concentration decreases from the
335 source to the POE, without taking into account any NP-dependent transport parameter. In this case
336 Eq. 12 is applied to calculate the HQ index using a constant value of RfD. However, this approach
337 is too simplistic, and size-dependent transport of the NPs from the source to POE must be
338 considered (Scenario B). As evidenced in Figure 2, taking into account the NP size-dependent
339 transport may result in significantly different values of HQ, even if the same NP mass at source is
340 considered.

341 Both in the case of application of the (simplistic) Scenario A, and of Scenario B, the definition of
342 RfD (and SF) values appropriate for NPs is likely the major challenge for the implementation of the

343 risk assessment procedure. Similarly to NP transport, also NP toxicity is known to be size
344 dependent. Toxicity studies on silver NPs provided different values of RfD for particles of different
345 size, particularly, higher toxicity for smaller particles (Kim et al., 2010; Windler et al., 2013;
346 Hadrup and Lam, 2014). Also the eventual coating may affect NPs toxicity: coating by humic acid
347 is reported to decrease toxicity of Silver NPs, while coating with citrate increases toxicity (Angel et
348 al., 2013).

349 Size-dependent toxicity profiles would be crucial for the correct application of risk assessment to
350 NPs. As reported for Scenario C in Figure 2, considering size-dependent RfD values, HQ may be
351 significantly different from the values obtained in Scenarios A and B. If size-dependent toxicity
352 values for NPs were available, a rigorous approach for the calculation of HQ and ILCR should take
353 into consideration the particle size distribution at POE, and the toxicity indexes should be obtained
354 by combining Eqs. 7-8 with Eqs. 12-13:

$$355 \quad HQ = \sum_i \left(\frac{C_{POE,i}}{RfD_i} \right) \cdot E = \sum_i \left(\frac{m_i \cdot N_{w,POE,i}}{RfD_i} \right) \cdot E \quad (14)$$

$$356 \quad ILCR = \sum_i (C_{POE,i} \cdot SF_i) \cdot E = \sum_i (m_i \cdot N_{w,POE,i} \cdot SF_i) \cdot E \quad (15)$$

357 Finally, the possible particle dissolution in the human body may also be an additional challenge
358 when evaluating NP-related risk to human health: for eg., some particles (eg. Silver NPs) may be
359 partly dissolved when ingested. For this reason, it would be recommended to calculate the risk
360 associated to ingestion using both the limits for NPs, and the limits for the corresponding dissolved
361 species.

362

363

364 **3. Application of the NP-modified risk assessment procedure**

365 **3.1 Methods**

366 The risk assessment procedure described in paragraph 2 was applied to a synthetic case of release of
367 Silver nanoparticles (Ag-NPs) from a landfill. The application followed these steps:

- 368 - Laboratory results from a published work on Ag-NP transport (Wang et al., 2014) were
 369 considered, and NP transport parameters were obtained by least-squares fitting the
 370 experimental breakthrough curves;
- 371 - The dependency of NP transport parameters on flow velocity and particle size was modeled
 372 following the approach of a previous work (Tosco et al., 2014) and transport parameters for
 373 the synthetic landfill test case were obtained from column test results; transport mechanisms
 374 were approximated to degradation and sorption processes, as discussed in paragraph 2.2;
- 375 - NP release from the landfill and transport in groundwater was simulated under Scenarios A
 376 and B of Figure 2 and toxic risk was estimated.

377

378 **3.1.1 Column tests**

379 Experimental results of column transport tests of Ag-NPs (average size $d_p=16$ nm) in natural soils
 380 reported by Wang et al. (2014), were modeled. In particular, two experimental breakthrough curves
 381 (BTCs) for Ag-NPs injected in pure quartz sand, and a mixture of 20% quartz sand and 80% of
 382 natural soil (average size $d_s=0.65$ mm for both quartz sand and soil) were considered, herein named
 383 "0%Soil" and "80%Soil", respectively. The NPs were injected at a concentration of 100 mg/l in
 384 fully saturated columns (inner diameter 1.1 cm, column length 10 cm, discharge rate 0.25 ml/min,
 385 porosity 0.42). The BTCs were inverse-fitted using the software MNMs
 386 (www.polito.it/groundwater/software/MNMs) (Tosco and Sethi, 2009; Bianco et al., 2016). Two
 387 linear interaction sites were considered, one irreversible (fitted parameter: $k_{a,irr}$) and one reversible
 388 (fitted parameters: $k_{a,rev}$ and $k_{d,rev}$). Thus Eqs. 7-8 become

$$\begin{cases}
 \frac{\partial}{\partial t}(\varepsilon N_{w,i}) + \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,irr,i}] + \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,rev,i}] + \nabla \cdot (uN_{w,i}) - \nabla \cdot (\varepsilon D \nabla N_{w,i}) = 0 \\
 \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,irr,i}] = \varepsilon k_{a,irr,i} N_{w,i} \\
 \frac{\partial}{\partial t}[(1-\varepsilon)N_{s,rev,i}] = \varepsilon k_{a,rev,i} N_{w,i} - k_{d,rev,i} (1-\varepsilon) N_{s,rev,i}
 \end{cases} \quad (16)$$

390 For the column tests, particles were assumed mono-dispersed and consequently only one class of
 391 NP size was considered ($i=1$). For the simulation of the release from the landfill, 20 classes were
 392 considered in Scenario B ($i=1, \dots, 20$).

393

394 **3.1.2 Modeling attachment/detachment parameters**

395 An approach similar to Tosco et al. (2014) was adopted to model the dependency of $k_{a,irr,i}$ and $k_{a,rev,i}$
396 from particle size and flow velocity. Briefly, the attachment rate is assumed proportional to the flow
397 velocity v and the deposition efficiency η_0 :

398
$$k_{a,i} = A_i v \eta_{0,i} \tag{17}$$

399 where A_j is an empirical coefficient which incorporates dependences on other parameters [L^{-1}].

400 The Yao model (Yao et al., 1971) was used to calculate $\eta_{0,i}$, which is function of several
401 parameters, including v and particle size.

402 Also the detachment rate depends on flow velocity (Tosco et al., 2014), thus

403
$$k_{d,i} = B_i v \tag{18}$$

404

405 **3.1.3 Synthetic test case of Ag-NP release from a landfill**

406 A landfill of longitudinal size $W=80$ m and transverse size $L_{gw}=80$ m subject to effective recharge
407 $I_{eff}=450$ mm/y was considered. The landfill is located above a 15 m thick unconfined aquifer, with
408 effective porosity $\varepsilon=0.2$, Darcy velocity $u=7.6 \cdot 10^{-7}$ m/s, longitudinal, transversal and vertical
409 dispersivities ($\alpha_x, \alpha_y, \alpha_z$) equal to 10, 3.3 and 0.5 m respectively. The concentration of NPs in
410 landfill waste and leachate may significantly vary among sites (Gottschalk et al., 2009; Sun et al.,
411 2014). In this work, $C_{leach}=15$ mg/l was assumed as representative value (Yang et al., 2012). No
412 attenuation was considered in the unsaturated zone for cautionary purposes, and only mixing with
413 groundwater (Eqs. S.3-S.4 in SI) was considered to obtain C_0 .

414 Exposure $E= 0.027$ l/kg/d was used following the ASTM standard, corresponding to residential use.
415 RfD was assumed constant for all particle classes, equal to $3.0 \cdot 10^{-2}$ mg/kg/d, based on the work of
416 Kim et al. (Kim et al., 2010).

417

418

419

420

421 **3.2. Results and Discussion**

422 **3.2.1 NP transport parameters: from column tests to simulated landfill release**

423 The experimental data of Wang et al. (2014) were first modeled using the dual site linear
424 attachment/detachment of Eq. 16 with $i=1$ (Figure 3 and Table 2). The two interactions mechanisms
425 (linear irreversible attachment and linear reversible attachment) were selected following a stepwise
426 approach, starting from the simplest model and increasing its complexity (and consequently number
427 of fitted parameters) until a satisfactory fitting of the experimental data was obtained. Briefly, the
428 simplest case of one linear irreversible interaction site (1 fitted parameter per each test, $k_{a,irr}$) was
429 considered the first option for both tests. However, the fitting was not satisfactory (data not
430 reported). The same for one linear reversible site (2 fitted parameters, $k_{a,rev}$ and $k_{d,rev}$). The third
431 option, namely linear irreversible attached associated to a second site of linear irreversible
432 attachment (3 parameters: $k_{a,irr}$, $k_{a,rev}$ and $k_{d,rev}$) was the simplest providing a good fitting, with R^2
433 parameter equal to 0.9888 and 0.8693 was obtained respectively for 0%Soil and 80%Soil. The fitted
434 attachment rate $k_{a,irr}$ for the first deposition mechanism (linear irreversible) is the same for both
435 column tests, while $k_{a,rev}$ and $k_{d,rev}$ for the second deposition mechanism (linear reversible) are
436 different. From a physical point of view, this finding suggests that irreversible attachment was not
437 affected by soil composition, but only by particle and soil size (and flow rate), and is therefore
438 likely related to NP mechanical retention. Conversely, reversible attachment also depends on soil
439 composition.

440 Eq. 17 was applied to fitted $k_{a,irr}$ and $k_{a,rev}$, Eq. 18 to fitted $k_{d,rev}$ obtained to determine the three
441 parameters A_{irr} , A_{rev} and B_{rev} . It is worth to mention that in the presence of linear (reversible or
442 irreversible) deposition, the attachment rate is independent of the injected concentration. As a
443 consequence, the parameters determined from these column tests (performed injecting Silver NPs at
444 a concentration of 100 mg/l) can be assumed valid for the simulation of the leaching landfill, where
445 the NP released concentration is 15 mg/l.

446 Two alternative approaches were then considered to simulate NP release from the landfill, among
447 those reported in Figure 2:

- 448 - Scenario A: NP size distribution was not considered; the released NPs are a homogeneous
449 samples of Silver NPs having the same size as those of the column tests (i.e. 16 nm);

450 - Scenario B: An NP size distribution was assumed, in the range 5 to 200 nm, divided into 20
451 classes, with same average particle size of Scenario A (16 nm). The particle size distribution
452 is reported in Figure 6 (blue curve at the source, i.e. $X = 0$).

453 In both Scenarios, the same mass of particles (15 g/l) was released.

454 The attachment and detachment rates ($k_{a,irr}$, $k_{a,rev}$ and $k_{d,rev}$) for the two Scenarios were calculated
455 using the values of A_{irr} , A_{rev} and B_{rev} (obtained from the column tests) in Eqs. 17-18. Following the
456 Yao model, the deposition efficiency (Figure 6), and consequently k_a , is a function, among other
457 parameters, of particle size and flow velocity; following Eq. 18, k_d is independent of particle size,
458 and is affected only by flow velocity. Consequently, for Scenario A, $k_{a,irr}$, $k_{a,rev}$ and $k_{d,rev}$ are
459 constant parameters, and the only difference compared to the column tests is due only to the
460 different flow velocity of the aquifer compared to the one applied in the column tests. For Scenario
461 B, a different set of $k_{a,irr,i}$ and $k_{a,rev,i}$ is obtained for each class, while $k_{d,rev}$ is constant for all classes.

462 The coefficients for both Scenarios are reported in Table 2.

463 Compared to the parameters fitted for column tests, the values obtained for Scenarios A and B for
464 the landfill synthetic case are roughly one order of magnitude lower, due to the different flow
465 velocity of column tests ($u=4.3 \cdot 10^{-5}$ m/s) and the landfill case ($u=7.6 \cdot 10^{-7}$ m/s). Also particle size
466 significantly influences the attachment/detachment coefficients: for Scenario B, $k_{a,irr,i}$ and $k_{a,rev,i}$
467 span over at least one order of magnitude, with particle size ranging from 15 to 200 nm, with
468 evident implications on the relevance of considering particle size distribution when simulating NP
469 transport (paragraph 2.2.1). These two findings both suggest the importance of considering
470 appropriate models and experimental conditions for the determination of NP transport parameters: if
471 a risk analysis for an NP release from a landfill similar to this test case is to be performed, it is
472 crucial to determine particle transport parameters from experiments performed as close as possible
473 to the real site conditions (eg. flow velocity and NP type and size). If such conditions cannot be
474 reproduced in the laboratory, appropriate, well-established relationships like those of Eqs. 17-18 are
475 to be applied to transfer the NP parameters to the field scale conditions.

476

477 **3.2.2 NP risk assessment**

478 The Domenico solution was then applied for the calculation of C_{POE} for the Ag-NPs in both
479 Scenarios A and B, and the modified ASTM procedure was applied for the risk assessment
480 (procedure fully described in SI in paragraph S2). The vertical extent of the mixing zone in the

481 aquifer (δ_{gw}) was calculated using Eq. S.4, resulting equal to 16.3 m (higher than the saturated
482 thickness b). As a consequence it was assumed $\delta_{gw}=b$ and vertical dispersion was neglected (Connor
483 et al., 2007). Mixing of leachate with groundwater resulted in a dissolved concentration at source
484 $C_0=3.08$ mg/l.

485 Applying the approximations discussed in paragraph 2.2.1, for both Scenarios A and B irreversible
486 deposition was simulated as a first order degradation, reversible deposition as a linear sorption. The
487 corresponding λ_i and R_i were calculated using the equations reported in Table 1 and are reported in
488 Table 2. The applicability of this approximation was verified using Eq. 11. For both Scenarios,
489 $Da>1$ is verified for any $x>8.2$ cm, thus allowing the application of Domenico's solution all over the
490 domain.

491 Transport in groundwater was simulated for Scenarios A and B in both transient and steady state
492 conditions to calculate the C_{POE} along the axis ($y=0, z=0$) where the highest concentrations are
493 found (Figure 4). Provided that the same concentration of Silver NPs is released at the source, under
494 Scenario A particles travel for a shorter distance: compare, for example, the concentration profiles
495 (left y-axis) along the plume axis at steady state in Figure 4 (to allow comparison of the two
496 Scenarios, the total mass concentration is here calculated for Scenario B using Eq. 3a). This
497 observed difference is due to the higher attachment efficiency, and consequently attachment rate,
498 characterizing 16 nm particles when compared to larger ones, which are present in the population of
499 Scenario B (see η_0 trend in Figure 6). Conversely, for Scenario B, particles as a whole travel for
500 longer distances, due to the presence of (few) larger particles having a lower attachment efficiency.

501 These observations have a direct impact on the results in terms of toxic risk. For Scenario A, Eq. 12
502 was directly applied to calculate HQ, since only one class of particles was considered. For Scenario
503 B, the Domenico solution was applied independently for each NP class, and Eq. 14 was then used to
504 calculate HQ, assuming that RfD is the same for all classes. HQ values along the x-axis are reported
505 in Figure 4. Being the retardation factor R higher for 80%Soil than for 10%Soil, in transient
506 conditions (namely, 5 years after the initial release from the landfill) the extent of the area with HQ
507 above the threshold limit of 1 is significantly higher for the 0%Soil, as it can be observed from both
508 concentration profiles along the plume axis (Figure 4), maps (Figure 5) and numerical values of
509 length and area with $HQ>1$ (Table S.1 in SI). However, the HQ at the steady state, which is usually
510 considered for risk assessment, is the same for both 0%Soil and 80%Soil, since the irreversible
511 attachment coefficient, and consequently the parameter λ , is the same, and the retardation
512 coefficient R has no influence on the steady state concentration (see paragraph A.2).

513 The results evidence that for Scenario B the overall mobility of the Ag-NP is higher, thus resulting
514 in larger areas where $HQ > 1$. For example, at steady state, HQ values higher than 1 are found up to
515 85.6 m for Scenario A and 98.2 m for Scenario B downgradient the source of contamination (Figure
516 5 and Table S.1). Correspondingly, the area having $HQ > 1$ is 16% larger for Scenario B compared to
517 Scenario A. This is due to the different transport of different classes of NPs, which are characterized
518 by different values of k_{aj} : the attachment efficiency (Figure 6) is higher for smaller particles, lower
519 for larger particles. As a consequence, larger particles travel for longer distances, and the original
520 particle size distribution at source (blue line in Figure 6) changes its shape along the x-axis,
521 showing a more pronounced decrease in the concentration of smaller particles compared to larger
522 ones. These results confirm that the adoption of size-dependent transport equations for NPs is worth
523 to be applied, even in a simplified Tier 2 approach, and that the direct application of Scenario A is
524 too simplistic.

525

526

527 **4. Conclusions**

528 The ASTM approach for the Tier 2 risk assessment procedure for contaminated sites has been here
529 adapted for application of releases of nanoparticles, and an example application to landfill leachate
530 was presented. Even if particle transport in porous media is a complex phenomenon, the governing
531 equations can be simplified under reasonable assumptions. It was demonstrated that particle
532 transport described by a combination of a linear reversible and a linear irreversible attachment can
533 be solved using the same equations of the transport of a dissolved contaminant subject to first order
534 degradation rate and linear sorption, provided that the time scale of the dynamic
535 attachment/detachment process is significantly smaller than the time scale of the transport in the
536 porous medium. Moreover, it was demonstrated that considering the size-dependent transport of
537 heterogeneous populations of NPs may lead to results, in terms of HQ values at POE, significantly
538 different compared to the simplistic model where the particle size dependent transport is not
539 considered. Similar considerations can be applied for other particle properties, eg. shape, surface
540 coating, etc., which have an impact on NP mobility in the subsoil, and the risk assessment
541 procedure for these cases could be the same here discussed for size-dependent particle transport.

542 Nevertheless, very few data are available at the moment on the influence of NP size, coating, shape
543 etc. on their toxicity (particularly, chronic toxicity, requested in risk analysis). This represents the

544 great challenge to the application of a risk assessment procedure to sites contaminated by
545 engineered nanoparticles. In this sense, the availability of size-dependent (or, more in general
546 parameter-dependent) reference doses is an unavoidable necessity, which has not been addressed at
547 the moment.

548 It is finally worth to mention that the standard ASTM procedure do not take into account particles
549 retained on the soil. However, it cannot be excluded that such NPs can be re-mobilized on a long
550 term (Navarro et al., 2014), following for eg. changes in groundwater hydrochemical conditions. As
551 a consequence, it is recommended that this issue is evaluated when dealing with sites contaminated
552 by NPs, and the possible release of deposited NPs on a long time scale is carefully evaluated and
553 eventually included in risk assessment scenarios.

554

555 **Acknowledgement**

556 The authors thank Mr. Federico Mondino for the collaboration in reviewing the literature on NP
557 toxicity. This research did not receive any specific grant from funding agencies in the public,
558 commercial, or not-for-profit sectors

559

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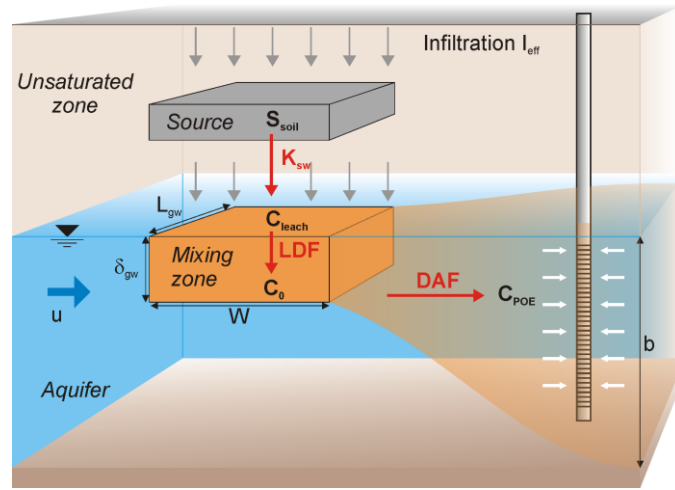
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725 **Figures**

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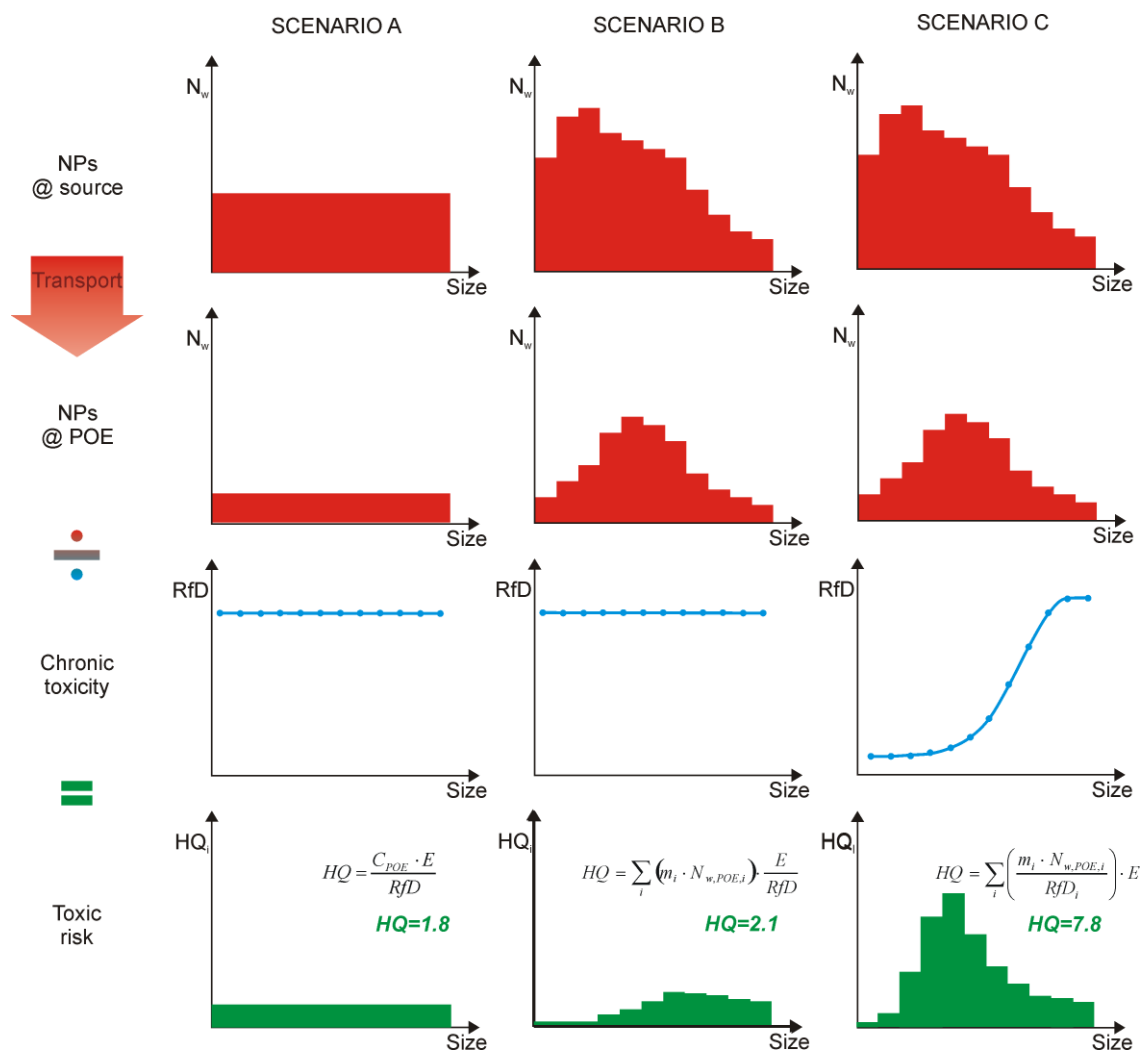
727 **Figure 1: Scheme of particle release and transport.**

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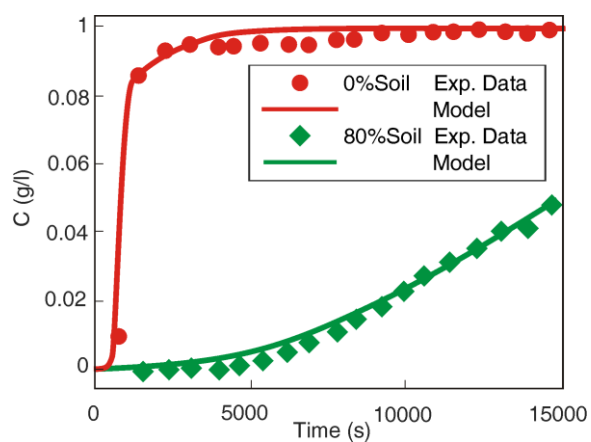
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Figure 2: Comparison of three different scenarios for the application of NP-adapted risk assessment procedure: Scenario A, assuming no size-dependent transport nor toxicity; Scenario B, assuming size-dependent NP transport; Scenario C, assuming size-dependent transport and toxicity. The released concentration is the same in all scenarios.

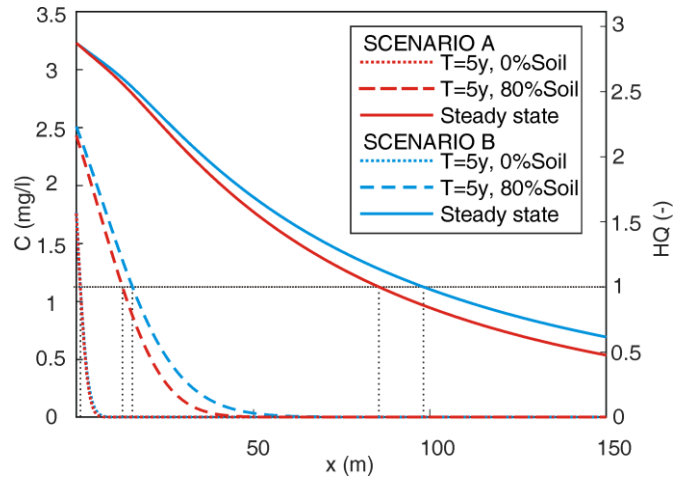


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Figure 3: Experimental and simulated Ag-NP breakthrough curves for the experimental data of Wang et al. (2014) for 0%Soil and 80%Soil tests.



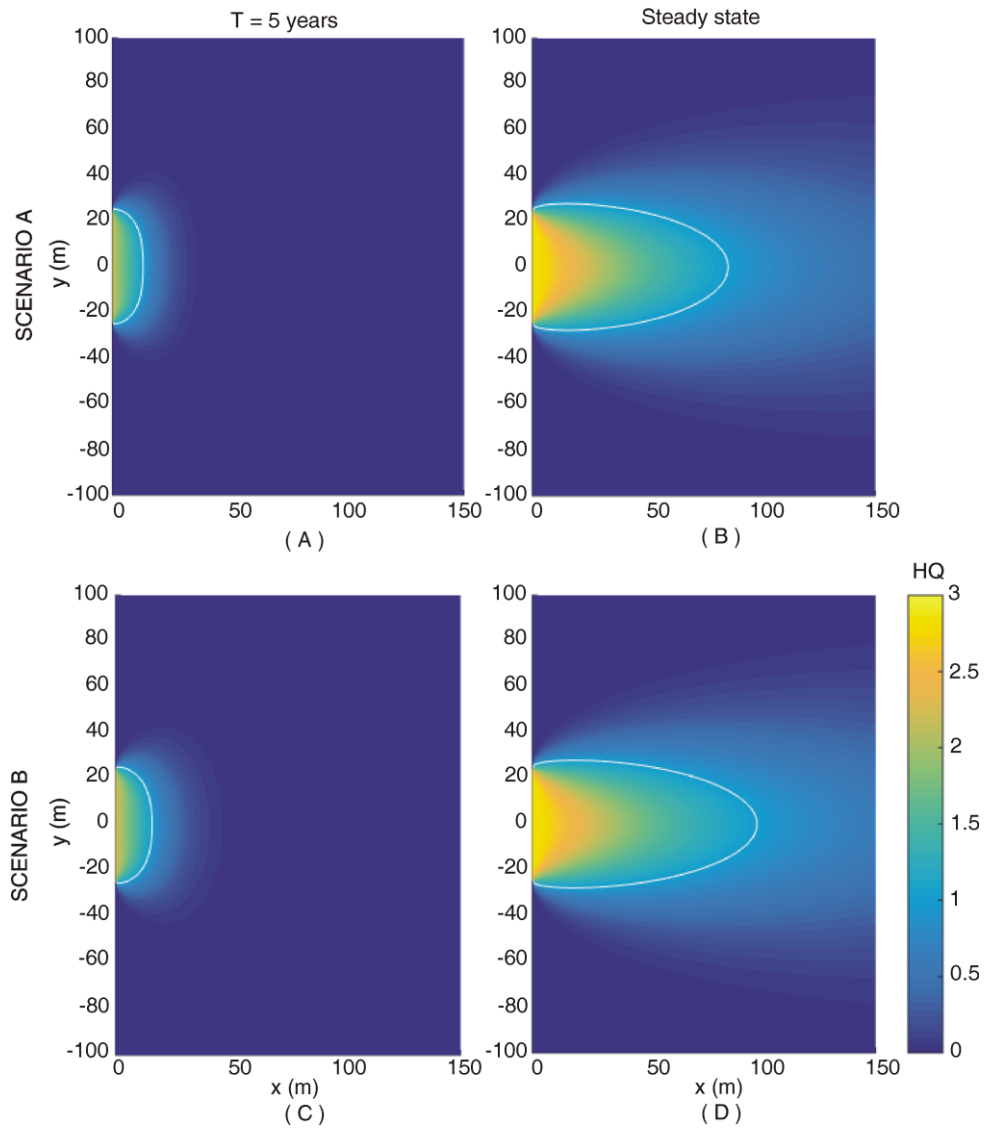
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741 **Figure 4: Synthetic test case for Ag-NPs release from a landfill: simulated Ag-NPs concentrations in**
 742 **groundwater and corresponding HQ values along the x axis ($y=0, z=0$) at steady state conditions (solid lines) and**
 743 **in transient conditions after 5 years for 0%Soil (dashed lines) and 80%Soil (dotted lines) for Scenario A (red)**
 744 **and Scenario B (blue).**

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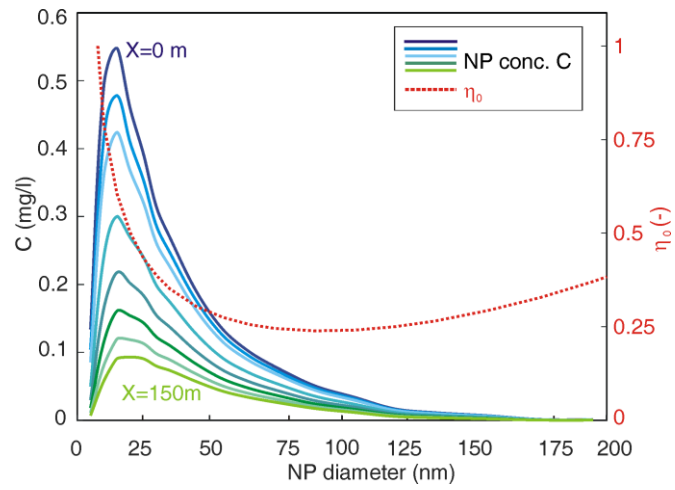


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749 **Figure 5: HQ maps calculated applying transient Domenico's solution after 5 years (Eq. S.6) for 0%Soil (A-C),**
 750 **and steady state solution (Eq. 6) (B-D). HQ is calculated assuming no size-dependent transport (A-B,**
 751 **corresponding to Scenario A in Figure 2) and size-dependent transport (C-D, corresponding to Scenario B in**
 752 **Figure 2).The white line corresponds to HQ=1.**

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756 **Figure 6: Synthetic test case for Ag-NPs release from a landfill: particle size distribution for Scenario B along the**
 757 **x axis $y=0, z=0$) at steady state, at different distances from the source (blue to green lines), and attachment**
 758 **efficiency as a function of particles size (red line).**

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761 **Tables**

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763 **Table 1: : Retention mechanisms for NP transport (1 or 2 interaction sites) and associated simplifying**
 764 **assumptions and parameter definition for the application of Domenico's solution**

Retention mechanism(s)		Simplifying assumptions	Definition of Domenico's parameters	Applicability of Domenico's solution	
				Transient (Eq. S.6)	Steady state (Eq. 6)
1 site linear $\psi_i = 1$	Irreversible $k_{d,i} = 0$	None	$\lambda_i = \varepsilon k_{a,i}$ $R_i = 1$	Yes	Yes
	Reversible $k_{d,i} \neq 0$	$\frac{1}{K_{eq,i}} \ll \frac{x}{v}$	$\lambda_i = 0$ $R_i = 1 + \frac{k_{a,i}}{k_{d,i}}$	Yes	Yes
1 site blocking $\psi_i = 1 - \frac{N_{s,i}}{N_{s,maxj}}$	Any (reversible or irreversible)	$\frac{1}{K_{eq,i}} \ll \frac{x}{v}$	$\lambda_i = 0$ R_i n.d.	No	Yes
2 sites	Site 1: linear irrev. Site 2: linear rev.	$\frac{1}{K_{eq,i}} \ll \frac{x}{v}$	$\lambda_i = \varepsilon k_{a1,i}$ $R_i = 1 + \frac{k_{a2,i}}{k_{d2,i}}$	Yes	Yes
	Site 1: linear irrev. Site 2: blocking	$\frac{1}{K_{eq,i}} \ll \frac{x}{v}$	$\lambda_i = \varepsilon k_{a1,i}$ R_i n.d.	No	Yes
	J=1 linear rev. J=2 blocking	$\frac{1}{K_{eq,i}} \ll \frac{x}{v}$	$\lambda_i = 0$ R_i n.d.	No	Yes

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767 **Table 2: Transport parameters for NPs in column tests and for the test case of Ag-NP release from a landfill**

Parameter	Column tests		Scenario A		Scenario B	
	0%Soil	80%Soil	0%Soil	80%Soil	0%Soil	80%Soil
Site 1						
Attachment rate k_{a1} (s^{-1})		$1.7 \cdot 10^{-7}$		$3.4 \cdot 10^{-8}$	$1.3 \cdot 10^{-8} - 7.0 \cdot 10^{-8}$	
Degradation rate $\lambda = \varepsilon \cdot k_{a1}$ (s^{-1})		$1.5 \cdot 10^{-8}$		$6.7 \cdot 10^{-9}$	$2.6 \cdot 10^{-9} - 1.4 \cdot 10^{-8}$	
Site 2						
Attachment rate k_{a2} (s^{-1})	$3.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-2}$	$5.9 \cdot 10^{-5}$	$2.0 \cdot 10^{-3}$	$2.3 \cdot 10^{-5} - 1.2 \cdot 10^{-4}$	$4.5 \cdot 10^{-3} - 1.0 \cdot 10^{-2}$
Detachment rate k_{d2} (s^{-1})	$7.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$
Retardation coeff. R (-)	1.4	21.0	12.8	562.0	5.6-25.4	222-1160

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