

Ecofriendly nanotechnologies and nanomaterials for environmental applications: Key issue and consensus recommendations for sustainable and ecosafe nanoremediation

*Original*

Ecofriendly nanotechnologies and nanomaterials for environmental applications: Key issue and consensus recommendations for sustainable and ecosafe nanoremediation / Corsi, I.; Winther-Nielsen, M.; Sethi, R.; Punta, C.; Della Torre, C.; Libralato, G.; Lofrano, G.; Sabatini, L.; Aiello, M.; Fiordi, L.; Cinuzzi, F.; Caneschi, A.; Pellegrini, D.; Buttino, I.. - In: ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY. - ISSN 0147-6513. - 154:(2018), pp. 237-244. [10.1016/j.ecoenv.2018.02.037]

*Availability:*

This version is available at: 11583/2784195 since: 2020-01-22T16:23:03Z

*Publisher:*

Elsevier

*Published*

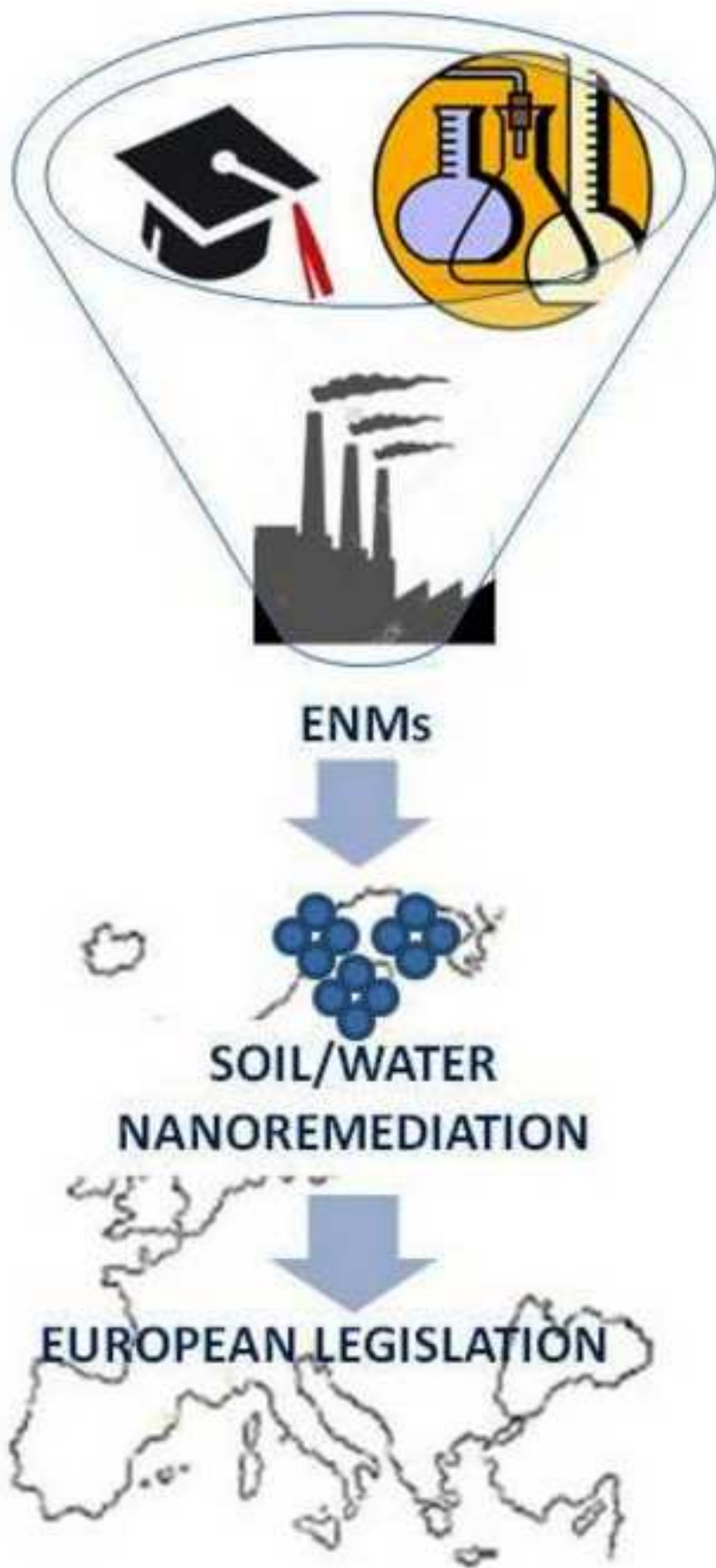
DOI:10.1016/j.ecoenv.2018.02.037

*Terms of use:*

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

*Publisher copyright*

(Article begins on next page)



## **Highlights**

- Nanotechnology represents a breakthrough for environmental remediation
- Ecosafety is a priority feature of ENMs intended for nanoremediation
- Predictive safety assessment of ENMs for environmental remediation is mandatory
- Greener and sustainable (nano) solutions are emerging
- Regulatory framework will support industrial competitiveness of the sector

1 ***Ecofriendly* nanotechnologies and nanomaterials for environmental applications:**  
2 **key issue and consensus recommendations for sustainable and ecosafe**  
3 **nanoremediation**

4

5 I. Corsi<sup>1\*</sup>, M. Winther-Nielsen<sup>2</sup>, R. Sethi<sup>3</sup>, C. Punta<sup>4</sup>, C. Della Torre<sup>5</sup>, G. Libralato<sup>6</sup>, G. Lofrano<sup>7</sup>,  
6 L. Sabatini<sup>8</sup>, M. Aiello<sup>9</sup>, L. Fiordi<sup>9</sup>, F. Cinuzzi<sup>10</sup>, A. Caneschi<sup>11</sup>, D. Pellegrini<sup>12</sup>, I. Buttino<sup>12\*</sup>

7

8 <sup>1</sup>Department of Physical, Earth and Environmental Sciences, University of Siena, via Mattioli, 4-53100 Siena, Italy

9 <sup>2</sup>Department of Environment and Toxicology, DHI, Agern Allé 5, 2970 Hoersholm, Denmark

10 <sup>3</sup>Department of Environment, Land and Infrastructure Engineering (DIATI), Politecnico di Torino, Italy

11 <sup>4</sup>Department of Chemistry, Materials, and Chemical Engineering “G. Natta”, Politecnico di Milano and RU INSTM,  
12 Via Mancinelli 7, 20131 Milano, Italy

13 <sup>5</sup>Department of Bioscience, University of Milano, via Celoria 26, 20133 Milano Italy

14 <sup>6</sup>Department of Biology, University of Naples Federico II, via Cinthia ed. 7, 80126 Naples, Italy

15 <sup>7</sup>Department of Chemical and Biology “A. Zambelli”, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano  
16 (SA), Italy

17 <sup>8</sup>Regional Technological District for Advanced Materials, c/o ASEV SpA (management entity), via delle Fiascaie 12,  
18 50053 Empoli (FI), Italy

19 <sup>9</sup>Acque Industriali SRL, Via Molise, 1 ,56025 Pontedera (PI), Italy

20 <sup>10</sup> LABROMARE SRL - Via dell'Artigianato 69, 57121 Livorno, Italy.

21 <sup>11</sup>Department of Chemistry & RU INSTM at the University of Firenze, Via della Lastruccia 3, 50019 Sesto F.no, Italy

22 <sup>12</sup>Institute for Environmental Protection and Research (ISPRA), Piazzale dei marmi 12, 57013 Livorno, Italy

23

24 **Key words:** nanoremediation; risk assessment; ecosafety; sustainability; nano-structured devices

25

26 Corresponding authors: both authors equally contributed to the manuscript.

27 \* Ilaria Corsi, [ilaria.corsi@unisi.it](mailto:ilaria.corsi@unisi.it);

28 \*Isabella Buttino, [isabella.buttino@isprambiente.it](mailto:isabella.buttino@isprambiente.it).

29

## Abstract

The use of engineered nanomaterials (ENMs) for environmental remediation, known as nanoremediation, represents a challenging and innovative solution, ensuring a quick and efficient removal of pollutants from contaminated sites. Although the growing interest in nanotechnological solutions for pollution remediation, with significant economic investment worldwide, environmental and human risk assessment associated with the use of ENMs is still a matter of debate and nanoremediation is seen yet as an emerging technology. Innovative nanotechnologies applied to water and soil remediation suffer for a proper environmental impact scenario which is limiting the development of specific regulatory measures and the exploitation at European level. The present paper summarizes the findings from the workshop :“Ecofriendly Nanotechnology: state of the art, future perspectives and ecotoxicological evaluation of nanoremediation applied to contaminated sediments and soils” convened during the Biannual ECOtoxicology Meeting 2016 (BECOME) held in Livorno (Italy). Several topics have been discussed and, starting from current state of the art of nanoremediation, which represents a breakthrough in pollution control, the following recommendations have been proposed : (i) ecosafety has to be a priority feature of ENMs intended for nanoremediation; ii) predictive safety assessment of ENMs for environmental remediation is mandatory; (iii) greener, sustainable and innovative nano-structured materials should be further supported; (iii) those ENMs that meet the highest standards of environmental safety will support industrial competitiveness, innovation and sustainability. The workshop aims to favour environmental safety and industrial competitiveness by providing tools and modus operandi for the valorization of public and private investments.

58 The application of nanotechnology includes the use of engineered nanomaterials (ENMs) to clean-  
59 up polluted media as soils, water, air, groundwater and wastewaters from which the current  
60 definition of *nanoremediation* (Karn et al., 2009; Lofrano et al., 2017a). Contamination by  
61 hazardous substances in landfills, oil fields, manufacturing and industrial sites, military installation  
62 including private properties represent a global concerns need to be remediated since it poses serious  
63 risk for health and well-being of humans and the environment (USEPA, 2004; PEN, 2015).

64 Compared to conventional *in situ* remediation techniques as thermal treatment, pump-and-treat,  
65 chemical oxidation including bioremediation which are almost known to be expensive, partially  
66 effective and time-consuming, nanoremediation has emerged as a new clean up method less costly,  
67 more effective as well as environmentally, socially, and economically sustainable (Otto et al. 2008,  
68 USEPA, 2013). In fact, nanotechnologies allow to treat contaminated media *in situ* and minimize  
69 the addition of further chemicals in the clean up process (Holland 2011). Nanoremediation relies on  
70 the peculiar properties of nanoscale particles or nanomaterials i.e. high reactivity and high surface  
71 area, which make them able to remove a wide spectra of hazardous environmental pollutants,  
72 including organoalogenated compounds (OA), hydrocarbons and heavy metals (Karn et al., 2009;  
73 Müller and Nowack 2010).

74 According to Project of Environmental Nanotechnology web site and USEPA, in the last ten  
75 years, almost 70 field scales worldwide have been successfully treated by using nanoremediation  
76 techniques, which in comparison with conventional methods have significantly reduced time frame  
77 (days vs months) and operational costs (up to 80%) (USEPA, 2009; PEN 2015).

78 Despite such promising expectations, nanoremediation has been slowly applied in Europe (JRC,  
79 2007) probably as a consequence of various factors as for instance the emerging societal worries on  
80 nanotechnologies and the current lack of regulatory and proper legislative supports (Nature  
81 Nanotechnology, 2007; Grieger et al., 2012).

82 The most applied nanoscale materials for nanoremediation are nano-scale zeolites, metal oxides,  
83 carbon nanotubes and noble metals have been demonstrated to cause several injuries in both  
84 terrestrial and aquatic organisms, thus certainly increasing governmental as well as public concerns  
85 related to their *in situ* application (Karn et al., 2009; see Table 1).

86 In Europe, it has been estimated that there are more than 2.5 million potentially polluted sites  
87 which need to be remediated and that 350,000 sites may cause a potential risk to humans or the  
88 environment (EEA, 2014). Here, the current debate relies on the balance between known benefits

89 and potential risks associated to the use of nano-scale materials in terms of mobility, persistency  
90 and ecotoxicity, other than on the current technical limitations in detection and monitor  
91 nanoparticles in the environment as well as in proper risk assessment procedures (Nowack et al.,  
92 2015).

93 The present paper summarizes the findings from the workshop :“Ecofriendly Nanotechnology:  
94 state of the art, future perspectives and ecotoxicological evaluation of nanoremediation applied to  
95 contaminated sediments and soils” convened during the Biannual ECOTOxicology Meeting 2016  
96 (BECOME) held in Livorno (Italy). Several topics have been discussed and, starting from current  
97 state of the art of nanoremediation, which represents a breakthrough in pollution control, the  
98 following recommendations have been proposed : (i) ecosafety has to be a priority feature of ENMs  
99 intended for nanoremediation; ii) predictive safety assessment of ENMs for environmental  
100 remediation is mandatory; (iii) greener, sustainable and innovative nano-structured materials should  
101 be further supported; (iii) those ENMs that meet the highest standards of environmental safety will  
102 support industrial competitiveness, innovation and sustainability. The workshop aims to favour  
103 environmental safety and industrial competitiveness by providing tools and modus operandi for the  
104 valorization of public and private investments. An overview of three European nanoremediation  
105 projects (i.e. two still ongoing) was presented with the aim to provide insights into the state of the  
106 art of collaborative research across Europe.

107

## 108 2. *State of the art of nanoremediation*

### 109 2.1 *Sediment/soil*

110 The quality of sediment and soil is an essential asset, being their remediation in case of pollution  
111 events, of extreme urgency. Oil spills, industrial and military activities, relevant accidents and  
112 incorrect or illegal waste management are the main responsible of sediment and soil contamination  
113 (Hurel et al., 2017). Their *ex situ* cleaning by mechanical removal of contaminated material or  
114 active *in situ* methods are often costly (Lofrano et al., 2017b; Libralato et al., 2018). Passive *in situ*  
115 approaches utilising engineered materials (EMs) (from the micro- to the nano-scale), which are  
116 deliberately introduced into the sediment/soil or delivered to surface water (e.g. oil spill), have  
117 shown to be potentially effective as catalytic agents, transforming contaminants into less harmful or  
118 harmless substances. However, *safe-by-design* is frequently unattended and environmental risk

119 assessment about nanoremediation is further away to be completed, even though some countries are  
120 already at the field scale (PEN, 2015).

121 Several papers, since the beginning of the nano-era, focused on the dichotomy of the effects of  
122 micro- (MP) and nano-sized particles (NP). Are NPs better than MPs? Of course, as usual, it  
123 depends. Costs and benefits are not always easy to define especially for emerging materials where  
124 the number of pros and cons are almost the same, at least at the beginning when unexplored aspects  
125 are still present, and contradictory results exist considering both human health and environmental  
126 effects (Lofrano et al., 2017b). Certainly, some concerns occur regarding the use of ENMs in  
127 contaminated soil/sediment: once dispersed in a contaminated site would ENMs be mobile to a  
128 point that they could be taken up by plants or animals at the site or further away, and adversely  
129 affect them? How to consider the environmental benefits and risks of ENMs for *in situ*  
130 applications? Does their use and behavior pose questions regarding environmental fate and impact?  
131 Do they provide easier and better results than the relative MPs? Moreover, a remediation  
132 technology must attend to cost-benefit approaches considering practical immediate issues and long-  
133 term expectancies. For example, nano-iron has an average cost of about 100 €/kg compared to 10  
134 €/kg of iron MPs (SiCon, 2016), mainly due to the relative economies of scale. The very high  
135 reactivity of iron NPs makes its *in situ* application sometimes difficult and the remediation activity  
136 could present a limited long-lasting ability (Grieger et al., 2010). Thus, a case-by-case analysis must  
137 be undertaken to assess the potential real applicability and need for nanoremediation.

138

140 Among emerging application of nanoremediation there is the global problem of marine  
141 contamination both in coastal and off-shore sites. Marine sediments are established as a major sink  
142 for environmental pollutants; the increasing number of sites to be remediated, together with  
143 significant times/costs of current technologies, are clearly promoting nanoremediation as a  
144 promising solution (Otto et al., 2008). However, sediment nanoremediation may pose a potential  
145 risk for marine biota, due to partial ENM mobilisation in interstitial waters and/or water column  
146 (Karn et al. 2009). This may affect not only sediment dwelling/deposit feeding species, but also  
147 other species from different trophic levels (bacteria, phyto-zooplankton, benthic invertebrates)  
148 (Kadar et al., 2012; Corsi et al., 2014; Minetto et al., 2016). An increasing number of ENM-based  
149 products are being developed specifically for marine applications as *in situ* nanoremediation. Some  
150 good examples are absorbent nanowires used for controlling and reducing the impact of oil spills  
151 (Yuan et al., 2008).

152 The risk associated with the release and accumulation of contaminants into the marine  
153 environment has been strongly faced with the development of an environmental risk assessment  
154 (ERA) framework. Past, but also recent, accidental marine pollution events have been handled by  
155 the application of ERA approaches and solved with a certain level of accuracy by linking the  
156 ecological effects to the physico-chemical nature of the stressor in terms of concentration-time-  
157 response relationship. A similar approach can be applied to the ENMs (Klaine et al., 2012) even  
158 though it needs to be tuned to “nano-specific” features as exposure and effect scenarios.

159 Exposure scenarios, as well as patterns of uptake and toxicity, are substantially still unknown for  
160 natural marine environment (Koelmans et al., 2015) and represent a major challenge for marine  
161 nano-ecotoxicologists and a hindrance for the use of ENMs in remediation. Bridging current  
162 knowledge acquired from lab-controlled experimental conditions to environmental realistic  
163 scenarios resembling natural ecosystems is therefore their featured mission (Gottschalk et al.,  
164 2013). This is further complicated by the general lack of appropriate methodologies able to detect  
165 and quantify ENMs in environmental matrices though some advancements are available for specific  
166 ENPs (Nowack et al., 2015).

167 The many peculiar features of ENMs as chemical core, size, shape and surface energy have been  
168 shown to substantially affect their final properties once released in complex natural environmental  
169 media as for instance sea water. In this context, marine waters are even more diverse since physico-  
170 chemical parameters, and inorganic and organic composition, substantially differ from surface,

171 column and deep waters as well as in lagoon, estuaries, coastal areas and deep oceans (Nowack et  
172 al., 2012).

173 The ENMs fate, in terms of dispersion, might be triggered by parameters as pH, osmolarity and  
174 natural organic matter (NOM) mainly based on colloids and proteins, which are able to interact with  
175 the specific properties of the ENM itself thus affecting uptake and toxicity in exposed organisms  
176 (Corsi et al., 2014). The outcome of such interactions is also affected by the biological status of the  
177 organism itself as for instance its ability to face and react to such exposure. Further effects could  
178 also be seen at higher level from organism, to population and community and the entire ecosystem  
179 (Matranga and Corsi, 2012).

180 In wastewater treatment nanotechnology emerged as a robust and efficient technology that  
181 overcomes the limits of existing processes, due to the tunable properties and outstanding features of  
182 ENMs (Qu et al., 2013). The main advances of nanotechnology applied to this sector rely in the  
183 ability to degrade almost completely several types of recalcitrant compounds (Shao et al., 2013;  
184 Lofrano et al., 2016). The three main applications are: i) nano-adsorbents: made of either carbon-  
185 based or metal-based NMs, such application has high efficiency on adsorption of organic pollutants  
186 and also for metal removal, due to extremely high specific surface area, more accessible sorption  
187 sites and lower intraparticle diffusion (Lofrano et al., 2016); ii) membrane systems based on  
188 nanofibers or nanocomposites, which offer a great opportunity to improve the membrane  
189 permeability, fouling resistance, mechanical and thermal stability, and to provide new functions for  
190 contaminant degradation (Liu et al., 2015); iii) nano catalysts, with focus on photocatalyst such as  
191  $\text{TiO}_2$  (Carotenuto et al., 2014; Lofrano et al., 2016). This application for the wastewater treatment  
192 allows fast and efficient removal of metals, and several types of organic pollutants such as for  
193 instance hydrocarbons, perfluorooctanoic acid, pharmaceuticals and personal care products as well  
194 as of antibiotic resistance bacteria and genes (Shao et al., 2013; Bethi et al., 2016).

195 Besides the potential of ENMs to improve the performance of existing water purification  
196 processes, nanotechnology would represent a major breakthrough towards the development of next-  
197 generation water supply systems, in which centralized water treatment facilities are supplemented  
198 with decentralized point-of-use (POU) infrastructures (Qu et al., 2013). Indeed, the application of  
199 nanotechnology-enabled devices, which could selectively remove specific class of contaminants,  
200 could allow the development of POU systems, which address the specific needs of local  
201 communities, allowing efficient wastewater treatment and reuse, boosting a more sustainable water  
202 supply (Qu et al., 2013). Based on the achievements obtained so far, nanotechnology holds great

203 potential as a tool for sustainable wastewater treatment and remediation. Nevertheless, most of the  
204 applications are still at laboratory scale, and some drawbacks for full scale application must be  
205 overcome, such as technical challenges related to the production of huge quantity of ENM/Ps, cost-  
206 effectiveness and environmental concerns related to their potential release (Lofrano et al., 2017a).

207 Future studies need to assess the applicability and efficacy of different nanotechnologies under  
208 more realistic conditions. For instance, most of the studies were based on relatively short time  
209 exposure periods, while the long-term performance of these nanotechnologies is largely unknown.  
210 Moreover, avoiding of unintended consequences on natural environments is the main issue for the  
211 effective adoption of this technology. In fact, the application of nanotechnology will inevitably lead  
212 to the release of ENMs in water and in sludge, from where they will likely enter natural ecosystems  
213 (Nogueira et al., 2015a). Currently several methods are available, mostly involving the exploitation  
214 of magnetic properties of some inorganic material, cross-flow filtration, and centrifugation.  
215 Recently great effort has been devolved to develop treatment systems with immobilized engineered  
216 nanoparticles (Delnavaz et al., 2015). Up to now few studies investigated the harmful effects of  
217 ENMs occurring in wastewater and sludge, highlighting a potential risk for wildlife, related to their  
218 application in wastewater processes (Carotenuto et al., 2014; Nogueira et al., 2015b).

219 The decrease in safe freshwater availability is one of the most challenging issue to be faced by  
220 many societies and the World in the 21<sup>st</sup> century. It can be ascribed to a series of factors such as the  
221 population growth, the effects of climate change on the hydrologic cycle, and the increasing  
222 pollution. Aquifer systems are depleting due to multiple problems such as overexploitation and salt  
223 water intrusion, inadequate sanitation, spread of common and emerging contaminants. If from one  
224 side nanotechnologies can be successfully used to treat the water after its exploitation (e.g. to  
225 remove salt and contaminants), the *in-situ* use of ENMs is a challenging, but very promising  
226 approach. Groundwater (or aquifer) nanoremediation, which exploits ENMs for the treatment of  
227 contaminated groundwater, broadens the range and increases the effectiveness of *in situ* remediation  
228 options. This approach can be very effective to treat contaminants very close to the source of  
229 pollution but, mainly due to the costs of reagents, it is not suitable to target widespread and areal  
230 contaminations such as those induced by saltwater intrusion or of agricultural origin (nitrates and  
231 phosphates). Several ENMs have been studied in the last years for groundwater remediation  
232 purposes. Even if the use of other materials has been explored, most of the particles which are  
233 currently being tested and show a good performance for groundwater remediation are iron-based  
234 nanoparticles, both in the form of iron particles alone, and as composite materials. Iron particles

235 include, e.g., nanoscale and microscale ZeroValent Iron (nZVI and mZVI) (Wang and Zhang,  
236 1997), and nano-sized iron oxides, such as goethite for heavy metals sorption, and ferrihydrite for  
237 improved microbial-assisted degradation of organic contaminants (Bosch et al., 2010). Examples of  
238 iron-based composite nanomaterials include CARBO-IRON®, where nZVI is embedded in a  
239 carbon matrix to promote mobility and contaminant targeting (Mackenzie et al., 2012), bimetallic  
240 particles, and emulsified zero valent iron (EZVI). Granular, millimetric zero-valent iron (ZVI) is  
241 one of the most successful reagents for groundwater remediation deployed in Permeable Reactive  
242 Barriers (PRBs). A PRB is a passive technology for *in situ* treatment of contaminated groundwater  
243 plumes (Di Molfetta and Sethi, 2006). Due to its capability of degrading a wide range of organic  
244 contaminants, and of reducing and immobilizing metal ions, ZVI has been employed in hundreds of  
245 PRBs worldwide. However, installation and construction limitations restrain the application of this  
246 technology, making the treatment of deep contaminations impracticable, for instance. Moreover,  
247 PRBs target only the dissolved plume and cannot be used for direct treatment of the source of  
248 contamination. Wang and Zhang (1997) proposed the use of nanoscale nZVI as an alternative to  
249 granular iron. Owing to its small particle size (less than 100 nm), nZVI is characterized by a high  
250 specific surface area (10-50 m<sup>2</sup>/g) and consequently exhibits a significantly faster contaminant  
251 degradation rate (Tosco et al., 2014). Furthermore, nZVI aqueous suspensions can be directly  
252 injected in the subsurface, directly targeting the plume close to the source of contamination and  
253 attaining higher depths than with PRBs. nZVI's small size and high reactivity alone, however, are  
254 not sufficient to ensure an effective remediation. In recent years, several laboratories worldwide  
255 have been seeking solutions to some of nZVI's main limitations, that must be addressed in regard to  
256 the effectiveness and feasibility in field-scale applications. They include in particular stability  
257 against aggregation, short and long-term mobility in aquifer systems, and longevity under  
258 subsurface conditions.

259 In the framework of the FP7 UE project AQUAREHAB (G.A. n. 226565) single and mixtures of  
260 guar gum and xanthan gum have been proved to be suitable for particle stabilization and delivery  
261 (Xue and Sethi, 2012; Aquarehab, 2014) while in NanoRem (FP7 EU funded project- Taking  
262 Nanotechnological Remediation Processes from the Lab Scale to End User Applications for the  
263 Restoration of a Clean Environment, G.A. n. 309517) a hybrid experimental and modeling  
264 procedure was developed in order to design pilot and full scale interventions. The procedure is  
265 supported by the softwares MNMs and MNM3D (Tosco et al., 2014b) that can be used to interpret  
266 the laboratory results and therefore to simulate important field parameters including particle

267 distribution, ROI, number of injection wells in the field. Understanding particle transport and  
268 deposition is of pivotal importance not only in the short term, during injection, but also in the long  
269 term, to understand the fate of the particles in the environment. Some particles, such as nZVI,  
270 usually are almost immobile under typical aquifer conditions, but other NMs can be significantly  
271 mobile in groundwater systems, eg. CarboIron and iron oxide NPs studied for metal immobilization  
272 in the framework of the H2020 REGROUND project (G.A. an. 641768) (Tirafferri et al., 2017). As a  
273 consequence, to guarantee the long-term safety of the remediation approach and meet regulatory  
274 requirements, it is of pivotal importance to provide reliable, quantitative estimations on the long-  
275 term mobility of the injected particles that may remain in the subsurface after reaction with the  
276 contaminant.

277

### 278 *3. Recommendations*

#### 279 *3.1 Ecotoxicological testing and predictive safety assessment tools*

280 To implement the effective application of nanotechnology, a thorough ecosafe predictive  
281 assessment approach should be performed addressing the following key aspects:

- 282 a) estimate the behavior of ENMs in the media to be remediated, with particular focus on  
283 the physico/chemical modifications induced by environmental factors, which might affect  
284 their reactivity and fate;
- 285 b) consider the nature of the pollutants and the characteristics of the polluted media/area and  
286 its surroundings;
- 287 c) identify possible toxicological targets of ENMs and provide a mechanism-based  
288 evaluation of ecotoxicity in different species and more important at ecosystem level.

289 Ecotoxicology can provide suitable tools able to select ecofriendly and sustainable ENMs for  
290 environmental remediation (Corsi et al., 2014). Together with the needs of a regulatory framework,  
291 the most important topics discussed during the workshop has been the absence of reproducible,  
292 standardized hazard testing methods for ENMs which is currently limiting the development of a  
293 safety risk assessment also for those intended for environmental application as nanoremediation  
294 (Zhou et al., 2016; Petersen 2015, Corsi et al., 2014; Kühnel and Nickel , 2014). Therefore, there is  
295 a urgent need to develop a comprehensive guidance on how to perform ecotoxicological testing of

296 ENMs in order to address current limitations and difficulties and support regulatory measures and  
297 environmental policies. Regulators expect to take decisions on the permitted level of ENMs  
298 released in the environment, as strongly required by stakeholders and industries. While  
299 standardized *ad hoc* ecotoxicity bioassays can be used as screening tools for selecting the best  
300 ecosafe design of ENMs used for remediation, any risk associated with their fate, behavior and  
301 interaction with biological components of the media under remediation should be carefully  
302 investigated by using a more ecosystem-scale approach.

303 Relevant environmental exposure scenarios which will include micro- and mesocosm studies and  
304 multi-trophic effects approach are thus particularly needed in order to address ENMs hazard at  
305 ecosystem level (Corsi et al., 2014). *Trojan horse* mechanism in cellular uptake of ENMs enhancing  
306 bioavailability and accumulation of contaminant to be remediated as well as its trophic transfer up  
307 to the food chain leading to biomagnification should be carefully considered and addressed by  
308 ecotoxicologists using an ecosystem-based approach. A more ecologically oriented hazard  
309 assessment of ENMs entering the natural environment has already been proposed and can take  
310 several advantages from the application in nanoremediation where size, properties and quantities of  
311 ENMs are known, as well as their potential biological effects from organism to population up to  
312 ecosystem level (Corsi et al., 2014). Therefore, the validation of standardized ecotoxicological  
313 testing methods as predictive safety assessment tools able to satisfy regulatory needs, should be the  
314 next EU target that will promote their eco-friendly application in remediation strategies.

315 Investigations of the most common used ENMs for remediation, nanoscale zero valent iron (nZVI)  
316 showed that it might cause hazardous effects to organisms in the environment, especially  
317 microorganisms (Grieger et al., 2010). A review of the recent published literature showed that  
318 although nZVI is a reactive substance with toxic properties, it could also stimulate microbiota  
319 through its influence on environmental parameters (Semerad and Cajthaml, 2016). Results show  
320 clearly that there is a need for further investigations to achieve a deeper understanding on how  
321 nZVI, as well as other ENMs applied for remediation, affect organisms in areas surrounding their  
322 applications. However, it should be considered that the purpose of *in-situ* nanoremediation is to  
323 reduce the toxic pollutants in a contaminated area and that the application of ENMs may reduce the  
324 overall toxicity of the contaminated site even if it has properties which could cause toxic effects on  
325 biota (Semerad and Cajthaml, 2016). Currently a certain level of uncertainty in risk assessment  
326 approaches is related to ENMs instability in water media, as for instance the tendency to form  
327 aggregates with different physical/chemical characteristics, with respect to the bare  
328 particles/materials (Lowry et al., 2012).

329 In order to optimize a remediation process, any potential fate scenarios need to be predicted from  
330 the ENM introduction into a polluted site until their removal or degradation upon elimination of the  
331 target pollutants (Stone et al., 2010; Nowack et al., 2012). Despite lack of methods for *in-situ*  
332 assessment of ENM speciation, ageing and agglomeration/aggregation state (Peijnenburg et al.,  
333 2016), predictive fate and transport models for ENMs are useful tools in the design and selection of  
334 a nanoremediation strategy for a specific contaminated area.

335 Different approaches have been used for describing the aggregation processes, which typical fall  
336 into two categories, one based on particle number (Praetorius et al., 2014) and another based on  
337 mass (Dale et al., 2015; Markus et al., 2015). The particle number based approach describes the  
338 aggregation kinetics using an attachment efficiency, a collision frequency and the particles  
339 concentrations, whereas in the mass based approach the attachment efficiency and collision  
340 frequency is replaced with a mass based rate of aggregation (Dale et al., 2015). The development of  
341 these models has primarily been driven by the need to understand the fate of ENMs in the  
342 environment and their possible environmental risk. Although deep insight on the environmental  
343 effect and fate of ENMs is still in its infancy, the model is able to compare and screen the impact of  
344 different ENMs when injected or dosed in a contaminated sediment layer. It is possible to apply the  
345 proposed concept to assess ENMs properties, which are crucial for their fate and transport. It can be  
346 used to explore the consequences of different input values such as pollutants, ENMs, salinity and  
347 sediment/soil properties. The concept provides the basic for ecosafe design of the ENM and choice  
348 of strategy for remediation (Figure 1).

349

### 350 3.2. Greener and sustainable (nano)solutions for remediation

351 While several ENMs reported in the literature show outstanding performances, in terms of  
352 decontamination efficiency of water and soil, the potential safety drawbacks related to their use in  
353 ecosystems, associated to possible bioaccumulation due to ingestion, dermal contact, and inhalation,  
354 are still controversial (Trujillo-Reyes et al., 2014). A multitude of studies have failed to reveal a risk  
355 of materials in the nano-dimension *per se*, as it is hard to differentiate ENMs effects to those of bulk  
356 materials (Laux et al., 2017). Nevertheless, under this uncertainty national and international  
357 regulations often adopt a conservative approach, banning the use of ENMs on field. This suggests  
358 the necessity to design new solutions, capable to take into account these critical aspects.

359 In this context, a valuable alternative strategy to overcome the ecotoxicology and legislative issues  
360 related to the use of ENMs for environmental remediation consists into the simple concept of  
361 moving from *nano-sized* materials to *nano-structured* devices, transferring the advantages of  
362 nanotechnology to macro-dimensioned systems. If ENMs, such as NPs and nanofibers, are not used  
363 directly in the remediation process, but become building blocks of stable nanostructured systems  
364 with enhanced micro- and nano-porosity, it is possible to provide a new class of sorbent units with  
365 high surface area, capable to remove organic and inorganic pollutants from contaminated water, air,  
366 and soil. To reach this goal, an optimized system should preserve the advantages deriving from  
367 ENMs and prevent their release in the ecosystem. Moreover, this approach could be considered  
368 even much more valuable if the new ENMs are obtained starting from the easy and scalable  
369 processing of renewable sources. For this reason, the choice of biopolymers as starting materials is  
370 becoming an important target.

371 Polysaccharides well fit most of the requirements for the design of ENMs, as they combine a good  
372 chemical reactivity for further nano-structuring processes, due to the presence of several hydroxyl  
373 functional groups on the polymer backbone, with their high biodegradability and negligible toxicity.  
374 Cellulose represents an abundant, renewable, and low-cost polysaccharide natural source, especially  
375 when deriving from agricultural and industrial by-products, for the production of materials for water  
376 remediation (Krishnani and Ayyappan, 2006). Sugarcane bagasse, fruit peel, biomass, and rice  
377 husks have been proposed as cellulose-based matrices for the removal of heavy metal ions from  
378 contaminated water. Moreover, waste paper would also represent an alternative, even cheaper  
379 source of cellulose, suggesting the virtuous approach of “*recycling to remediate*” (Setyono and  
380 Valiyaveetil, 2016).

381 Nevertheless, what makes cellulose so attractive as source for the design of advanced materials is  
382 its intrinsic hierarchical structure (Kim et al. 2015). The cellulose fiber composite is made with  
383 macrofibers of cellulose, hemicellulose and lignin. The macrofibers are composed of microfibrils,  
384 which in turn are formed with nanofibrils of cellulose. The possibility to cleave the original  
385 structure of native cellulose and to produce cellulose nanofibers (CNF) opens interesting  
386 perspectives for a wide range of applications, including wastewater treatment. Following the  
387 simplest protocol to produce CNF, cellulose can be preliminary oxidized with the 2,2,6,6-  
388 tetramethylpiperidinyloxy (TEMPO)-mediated system (Pierre et al., 2017), selectively converting  
389 primary C6-hydroxyl groups of the glucose units to the corresponding carboxylic groups.  
390 According to this procedure, defibrillation of TEMPO-oxidized cellulose nanofibers (TOCNF) can

391 be achieved by increasing the pH of the solution. In fact, the deprotonation of carboxylic groups  
392 favor the electrostatic repulsion of negatively charged single fibrils, leading to the physical  
393 separation of single fibriles. Hydrogels obtained from TOCNF have been reported as efficient and  
394 reusable adsorbents of heavy metal ions (Isobe et al., 2013). However, TOCNF can be also used for  
395 further cross-linking, taking advantage of the new carboxylic moieties introduced on the polymer  
396 backbone. While this process would lead to macro-dimensioned nano-structured systems, with all  
397 the advantages previously discussed, the choice of the ideal cross-linker would allow to introduce  
398 additional properties and functional groups, increasing the versatility of the systems. In this context,  
399 we recently reported a thermal route for the production of a new class of aerogels, starting from  
400 TOCNF and following a simple thermal protocol in the presence of branched-polyethyleneimine  
401 (bPEI) (Melone et al., 2015a). The formation of amide bonds between the carboxylic and the amine  
402 moieties favored the high reticulation into sponge-like, water stable systems, which show high  
403 efficiency in removing heavy metals and phenolic derivatives from wastewater. The possibility to  
404 functionalize selectively the amino groups of the cross-linker (Melone et al., 2015b), and to use  
405 these devices as templates for further organic (Panzella et al., 2016) and inorganic (Melone et al.,  
406 2013) coating, suggests the potentialities of this new ENM, whose properties can be modulated in  
407 order to perform selectively for the absorption and degradation of target contaminants. Moreover,  
408 the implementation of these systems for biomedical applications in the field of drug-delivery  
409 (Fiorati et al., 2017) enforce their safe use for environmental remediation.

410 In the framework of the NANOBOND project (Nanomaterials for Remediation of Environmental  
411 Matrices associated to Dewatering), the specific application of hydrogels obtained from TOCNF  
412 and tested for their ecosafety will aim to develop new ecofriendly nanotechnologies for sludge and  
413 dredged sediment remediation. Funded in the framework POR CReO FESR Tuscany 2014-2020,  
414 the NANOBOND project aims to develop an innovative system for treating contaminated sludge  
415 and dredged sediments, by coupling the use of nanostructured *eco-friendly* materials with the  
416 classical geotextile dewatering tubes. This new solution, will enable to reduce contaminated sludge  
417 and sediments, in terms of volumes and costs of transport, but also to convert the resulting solid and  
418 liquid wastes to a renewable clean resource to be use, for instance, in riverbanks settlements and  
419 any other applications. By developing nanoremediation techniques associated with dewatering,  
420 NANOBOND intends to explore new solutions to dredging and sludge management linked to  
421 hydrogeological disruption and maintenance of harbour areas, emerging issues which are  
422 tremendously increasingly worldwide. This innovative solution aims to become an efficient strategy

423 to significantly reduce sludge and sediment contamination through nanoremediation since also  
424 easily scalable for large-scale *in situ* applications with competitive costs. The NANOBOND  
425 consortium made by a 70% of industrial partnership specifically of companies involved in sludge  
426 and dredged sediment disposal as well as in their risk assessment and 30% of academia and research  
427 institutes for synthesis, ecosafety and life cycle assessment of nanostructured materials  
428 accomplished the requirements of technology transfer and business development needed for the  
429 development of an ecosafe and sustainable nanoremediation and promote economic development in  
430 terms of industrial competitiveness and innovation, both still very little developed in European  
431 countries.

432 Further examples include the INTERREG EUROPE project TANIA (TreAting contamination  
433 through NanoremedIAtion) with the aim to improve EU regional policies on treating contamination  
434 through nanoremediation in European countries and to implement regional development policies in  
435 the field of the environmental prevention and protection by pollutants. TANIA specifically  
436 addresses innovative and low cost technological solutions for the (nano)remediation of  
437 contaminated soil and water.

438 Green nanotechnology refers to the use of nanotechnology to enhance the environmental  
439 sustainability of processes producing negative externalities. It also refers to the use of  
440 nanotechnology products to enhance sustainability. It includes making green nano-products and  
441 using nano-products in support of sustainability.

442

### 443 *3.3. Environmental safety and industrial competitiveness*

444 In the field of environmental remediation and the related treatments and disposal of the various  
445 solid and liquid matrices, strong collaboration between industrial sector and research is absolutely  
446 needed. Specific issues related to waste or site typologies and the resulting innovation from the  
447 applied nanotechnologies and their development, will increase the competitiveness of companies  
448 involved in the environmental sector with also benefit from applied research as the increase of  
449 patents. A role that must be played together by researchers and industries is in the choice of  
450 strategies that will allow the scale-up of the material and techniques developed, taking in mind that  
451 the amount of materials to be employed is measured in tons or kilotons, as like as the cost of  
452 production must be affordable for concretely tackle large scale case. This aspect not necessarily  
453 must be considered as mass production because it can also have success with an approach for niche

454 production, but for sure the valley between the laboratory bench production and an industrial  
455 product ready for commercialization must be cross, keeping in mind all the classical problems that  
456 this pathway usually meets. A multidisciplinary approach must be applied at the forefront of the  
457 most advanced nanotechnological solutions to be tunable according to different situations.

458 Remediation should accomplish several aspects according to national regulation, human and  
459 environmental safety and contract management economics.

460 The global nanotechnology market in environmental applications reached \$23.4 billion in 2014.  
461 This market is expected to reach about \$25.7 billion by 2015 and \$41.8 billion by 2020, registering  
462 a compound annual growth rate (CAGR) of 10.2% from 2015 to 2020  
463 ([https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-](https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-applications-market-nan039c.html)  
464 [applications-market-nan039c.html](https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-applications-market-nan039c.html)). The urgent need to develop commercially-deployed  
465 remediation technologies at European level have seen the involvement of service providers and site  
466 owners or managers which are now finally considering their potential applications as well as  
467 implications for their business activities.

468 In terms of land, this solution accounts for 50% of land reclamation, while technological  
469 processing solutions represent minority percentages (EEA, 2012). In the case of dredged sediment  
470 management, the traditional approach involves storing in collapsed crates or CDF (Confined  
471 Disposal Facility), capping or conferral in a controlled landfill.

472 An increase of sustainable environmental remediation solution is therefore mandatory so that the  
473 benefit of the remediation action will be greater than the impact of the action itself (SuRF Italy,  
474 2014). This is particularly evident in recovery of former industrial areas, which, apart from limiting  
475 soil consumption, can produce benefits beyond the cost of the interventions themselves. Today,  
476 more than ever, these interventions become significant given the wide presence of dismantled  
477 industrial areas, transformed into large "urban voids", following the progressive outsourcing of  
478 western economies.

479 The approach to re-use (both the areas to be reclaimed and the environmental matrices) is the aim  
480 of numerous studies that highlight the possibilities of recovery. In the case of dredged sediments,  
481 for instance, recovery is possible by using them as materials in the building industry (Hamer et al.,  
482 2005) or as infrastructural components using geotubes (Sheehana and Harringtonb, 2012).

483 The European Community promotes the more efficient use of resources: in the logic of the  
484 circular economy, the circle closes with the transformation of waste into resources (European  
485 Commission, 2014). The innovative approach of the circular economy aims to bring greater

486 resource efficiency and material savings, based on the life cycle principle (Kobza and Schuster,  
487 2016).

488

#### 489 4. *Concluding remarks*

490 As the potential and efficacy of nanotechnology is well established, several drawbacks related to  
491 the full-scale application should be overcome. In particular great efforts should be devoted to  
492 develop innovative, green and sustainable (nano)solutions, which own ecosafe features such as  
493 limited mobility in environmental media and no toxicological effects for humans and wildlife.

494 To further promote the application of nanoremediation regional policy makers must work together  
495 and with main stakeholders in order to: (i) support research and innovation for identification of  
496 ecosafe and sustainable (nano)solutions; (ii) define a standardized methodology to evaluate ENMs  
497 effectiveness, ecosafety and economic sustainability within the context of existing environmental  
498 regulations at National and European level; (iii) support patenting and pilot applications of new  
499 ENMs developed on the basis of ecosafety by design concepts; (iv) develop a policy framework to  
500 provide incentives for *in-situ* use of ENMs for treatment of contaminated soil and water; (v) raise  
501 awareness on the process of nanoremediation, its benefits and means of application. In this context  
502 ecotoxicology, as well as predictive models, can be extremely helpful in risk assessment for  
503 regulatory needs. Greener and sustainable solutions as *ecofriendly* (nano)materials will be also  
504 mandatory for supporting industrial competitiveness, innovation and sustainability of the sector. A  
505 specific legislation at European level is necessary to regulate their emissions and field application.

506 Overall, the generation of ENMs that meet the highest standards of environmental safety will  
507 therefore support the effective deployment of nanoremediation at European and international level.

508

509

510

511

512

513        **Acknowledgements**

514        This work was partially supported by the project NANOBOND (Nanomaterials for Remediation  
515 of Environmental Matrices associated to Dewatering, Nanomateriali per la Bonifica associata a  
516 Dewatering di matrici ambientali) POR CReO FESR Toscana 2014-2020 - 30/07/2014- LA 1.1.5  
517 CUP 3389.30072014.067000007 and by the performance contract with the Danish Ministry of  
518 Higher Education and Science.

519

520

521

522

523 **References**

- 524 Aquarehab, 2014. Injectable reducing iron particles - Generic guideline. FP7 Collaborative project,  
525 G. A. n. 226565.  
526
- 527 Baun A., Hartmann N.B., Grieger K., Kusk K.O., 2008. Ecotoxicity of engineered nanoparticles to  
528 aquatic invertebrates: a brief review and recommendations for future toxicity testing.  
529 *Ecotoxicology* 17, 387–395  
530
- 531 Bethi B., Sonawane S.H., Bhanvase B.A., Gumfekar S.P. 2016. Nanomaterials-based advanced  
532 oxidation processes for wastewater treatment: A review. *Chem. Engineer. Proc.* 109, 178–189.  
533
- 534 Bosch J., Heister K., Hofmann T., Meckenstock R.U. 2010. Nanosized iron oxide colloids strongly  
535 enhance microbial iron reduction. *Appl. Environ. Microbiol.* 76, 184-189.  
536
- 537 Carotenuto M., Lofrano G., Siciliano A., Alberti F., Guida M. 2014. TiO<sub>2</sub> photocatalytic  
538 degradation of caffeine and ecotoxicological assessment of oxidation by-products. *Global NEST J.*  
539 16, 463-473.  
540
- 541 Corsi I., Cherr G.N., Lenihan H.S., Labille J., Hasselov M., Canesi L., Dondero F., Frenzilli G.,  
542 Hristozov D., Punes V., Della Torre C., Pinsino A., Libralato G., Marcomini A., Sabbioni E.,  
543 Matranga V. 2014. Common Strategies and Technologies for the Ecosafety Assessment and  
544 Design of Nanomaterials Entering the Marine Environment. *ACS Nano* 8, 9694-709.  
545
- 546 Dale A.L., Lowry G.V., Casman E.A. 2015. Much ado about  $\alpha$ : reframing the debate over  
547 appropriate fate descriptors in nanoparticle environmental risk modeling. *Environ. Sci. Nano.* 2,  
548 27-32.  
549
- 550 Delnavaz M., Ayati B., Ganjidoust H., Sanjabi S., 2015. Application of concrete surfaces as novel  
551 substrate for immobilization of TiO<sub>2</sub> nano powder in photocatalytic treatment of phenolic water.  
552 *J. Environ. Health Sci. Engineer.* 13, 1-20.  
553
- 554 Di Molfetta A. and Sethi R. 2006. Clamshell excavation of a permeable reactive barrier. *Environ.*  
555 *Geol.* 50, 361-369.  
556
- 557 European Commission 2014. Towards a circular economy: A zero waste programme for Europe.  
558 COM (2014) 398 final/2, pp. 16.  
559
- 560 EEA-European Environment Agency 2012. European Environment Information and Observation  
561 Network (EIONET).  
562
- 563 EEA-European Environment Agency 2014. Progress in management of contaminated sites. Report  
564 CSI 015. Copenhagen, Denmark. Available: [http://www.eea.europa.eu/data-and-](http://www.eea.europa.eu/data-and-maps/indicators/progress-in-management-of-contaminated-sites-3/assessment)  
565 [maps/indicators/progress-in-management-of-contaminated-sites-3/assessment](http://www.eea.europa.eu/data-and-maps/indicators/progress-in-management-of-contaminated-sites-3/assessment).  
566
- 567 Fiorati A., Turco G., Travan A., Caneva E., Pastori N., Cametti M., Punta C., Melone L. 2017.  
568 Mechanical and drug release properties of sponges from cross-linked cellulose nanofibers. *Chem.*  
569 *Plus. Chem.* 82, 848-858.  
570

571 Gottschalk F., Sun T., Nowack B. 2013. Environmental concentrations of engineered  
572 nanomaterials: Review of modeling and analytical studies. *Environ. Pollut.* 181, 287–300.  
573

574 Grieger, K.D., Fjordbøge, A., Hartmann, N.B., Eriksson, E., Bjerg, P.L. & Baun, A. 2010.  
575 Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation:  
576 risk mitigation or trade-off? *J. Cont. Hydrol.* 118, 165–83.  
577

578 Grieger, K, Wickson, F, Andersen, HB. and Renn, O. 2012. Improving risk governance of emerging  
579 technologies through public engagement: the neglected case of nano-remediation? *Int. J. Emerg.*  
580 *Technol. Soc.* 10, 61-78.  
581

582 Hamer K., Hakstege P., Arevalo E. 2005. Treatment and disposal of contaminated dredged  
583 sediments. In: Lens P., Grotenhuis T., Malina G., Tabak H., *Soil and Sediment Remediation.*  
584 *Mechanisms, technologies and applications.* London (UK): IWA Publishing, 345-369.  
585 <http://www.enveurope.com/content/26/1/4>.  
586

587 Holland K.S. 2011. A framework for sustainable remediation. *Environ. Sci. Technol.* 45, 7116–  
588 7117.  
589

590 Hurel C., Taneez M., Volpi Ghirardini A., Libralato G. 2017. Effects of mineral amendments on  
591 trace elements leaching from pre-treated marine sediment after simulated rainfall events. *Environ.*  
592 *Poll.* 220, 364-374. doi: 10.1016/j.envpol.2016.09.072.  
593

594

595 Isobe N., ChenX., KimU.-J., KimuraS., Wada M., SaitoT., Isogai A. 2013. TEMPO-oxidized  
596 cellulose hydrogel as a high-capacity and reusable heavy metal ion adsorbent. *J. Hazard. Mater.*  
597 260, 195-201.  
598

599 Joint Research Centre (JRC) 2007. Report from the Workshop on Nanotechnologies for Envi-  
600 ronmental Remediation. JRC Ispra 16-17 April 2007. David Rickerby and Mark Morrison.  
601 [www.nanowerk.com/nanotechnology/reports/reportpdf/report101.pdf](http://www.nanowerk.com/nanotechnology/reports/reportpdf/report101.pdf)  
602

603 Kadar E., Dyson O., Handy R.D. & Al-Subiai S.N., 2012. Are reproduction impairments of free  
604 spawning marine invertebrates exposed to zero-valent nano-iron associated with dissolution of  
605 nanoparticles? *Nanotoxicology* 1-9.  
606

607 Karn B., Kuiken T., Otto M. 2009. Nanotechnology and in Situ Remediation: A Review of the  
608 Benefits and Potential Risks. *Environ. Health Perspec.* 117, 1823-1831.  
609

610

611 Klaine S.J., Koelmans A.A, Horne N., Carley S., Handy R.D., Kapustka L., Nowack B., von der  
612 Kammer F. 2012. Paradigms to assess the environmental impact of manufactured nanomaterials.  
613 *Environ. Toxicol. Chem.* 31, 3–14.  
614

615 Kobza N. and Schuster A. 2016. Building a responsible Europe, the value of circular economy.  
616 *IFAC* 49, 111–116.  
617

618 Koelmans A.A., Diepens, N.J., Velzeboer I., Besseling E., Quik J.T.K., van de Meent D. 2015.  
619 Guidance for the prognostic risk assessment of nanomaterials in aquatic ecosystems. *Sci. Tot.*  
620 *Environ.* 353, 141-149.  
621

622 Krishnani K.K., Ayyappan S. 2006. Heavy metals remediation of water using plants and  
623 *lignocellulosica* growastes. *Rev. Environ. Contam. Toxicol.* 188, 59-84.  
624

625 Kühnel D., Nickel C. 2014. The OECD expert meeting on ecotoxicology and environmental fate —  
626 Towards the development of improved OECD guidelines for the testing of nanomaterials – *Sci.*  
627 *Tot. Environ.* 472, 347–353.  
628

629 Yuan J., Liu X., Akbulut O., et al. 2008. Superwetting nanowire membranes for selective  
630 absorption. *Nature Nanotechnol.* 3, 332–336.  
631

632 Laux P., Tentschert J., Riebeling C., Braeuning, A., Creutzenberg, O., Epp A., Fessard V., Haas K.-  
633 H., Haase A., Hund-Rinke K., Jakubowski N., Kearns P., Lampen A., Rauscher H., Schoonjans  
634 R., Störmer A., Thielmann A., Mühle U., Luch A. 2017. Nanomaterials: certain aspects  
635 of application, risk assessment and risk communication. *Arch. Toxicol.*  
636

637 Libralato, G., Minetto, D., Lofrano, G., Guida, M., Carotenuto, M., Aliberti, F., Conte, B.,  
638 Notarnicola, M. (2018). Toxicity assessment within the application of in situ contaminated  
639 sediment remediation technologies: A review. *Sci. Tot. Environ.* 621, 85-94.  
640

641 Liu Q., Zheng Y., Zhong L., Cheng X. 2015. Removal of tetracycline from aqueous solution by a  
642 Fe<sub>3</sub>O<sub>4</sub> incorporated PAN electrospun nanofiber mat. *J. Environ. Sci.* 28, 29–36.  
643

644 Lofrano G., Carotenuto M., Libralato G., Domingos R.F., Markus A., Dini L., Gautam R.K.,  
645 Baldantoni D., Rossi M., Sharma S.K., Chattopadhyaya M.C., Giugni M., Meric S., 2016.  
646 Polymer functionalized nanocomposites for metals removal from water and wastewater: An  
647 overview. *Water Res.* 92, 22-37.  
648

649 Lofrano G., Libralato G., Brown J. 2017a. *Nanotechnologies for Environmental Remediation -*  
650 *Applications and Implications*, Springer.  
651

652 Lofrano G., Libralato G., Minetto D., De Gisi S., Todaro F., Conte B., Calabrò D., Quatraro L.,  
653 Notarnicola M. 2017b. *In situ* remediation of contaminated marine sediment: an overview.  
654 *Environ. Sci. Pollut. Res.* 24, 5189 -5206.  
655

656 Lowry G. V., Gregory K. B., Apte S. C., Lead J. R. 2012. Transformations of nanomaterials in the  
657 environment. *Environ. Sci. Technol.* 46, 6893-9.  
658  
659

660 Ma H., Williams P.L. , Diamond S.A., 2012. Ecotoxicity of manufactured ZnO nanoparticles: A  
661 review. *Env. Pollut.* 172, 76-85.  
662

663 Mackenzie K., Bleyl S., Georgi A., Kopinke F.D. 2012. Carbo-Iron - An Fe/AC composite - As  
664 alternative to nano-iron for groundwater treatment. *Wat. Res.* 46, 3817-3826.  
665

666 Markus A.A., Parsons J.R., Roex E.W.M, de Voogt P., Laane R.W.P.M. 2015. Modeling  
667 aggregation and sedimentation of nanoparticles in the aquatic environment. *Sci. Tot. Environ.*  
668 506-507, 323-329.  
669

670 Matranga, V., Corsi, I. 2012. Toxic effects of engineered nanoparticles in the marine environment:  
671 model organisms and molecular approaches. *Mar. Environ. Res.* 76, 32–40.  
672

673 Melone L., Altomare L., Alfieri I., Lorenzi A., De Nardo L., Punta C. 2013. Ceramic aerogels from  
674 TEMPO-oxidized cellulose nanofibre templates: Synthesis, characterization, and photocatalytic  
675 properties. *J. Photochem. Photobiol. A.* 261, 53-60.  
676

677 Melone L., Rossi B., Pastori N., Panzeri W., Mele A., Punta, C. 2015a. TEMPO-oxidized cellulose  
678 cross-linked with branched polyethyleneimine: Nanostructured adsorbent sponges for water  
679 remediation. *Chem. Plus. Chem.* 80, 1408-1415.  
680

681 Melone L., Bonafede S., Tushi D., Punta C., Cametti M. 2015b. Dipincolorimetric fluoride sensing  
682 by a chemically engineered polymericcellulose/bPEI conjugate in the solid state. *RSC Adv.* 5,  
683 83197-83205.  
684

685 Minetto D., Volpi Ghirardini A., Libralato G., 2016. Salt water ecotoxicology of Ag, Au, CuO,  
686 TiO<sub>2</sub>, ZnO, C60 engineered nanoparticles: an overview. *Env Int.* 92-93, 189-201.  
687

688 Müller N.C. and Nowack B. 2010. Nano Zero Valent Iron – the solution for water and soil  
689 remediation? ObservatoryNANO Focus Report.  
690

691 NanoRem, 2017. <http://www.nanorem.eu/Displaynews.aspx?ID=824> (12th March 2017 7.16 pm).  
692

693 Nature Nanotechnology, 2007. A little Knowledge. Editorial, 12, 731.  
694

695 Nogueira V., Lopes I., Rocha-Santos T., Goncalves F., Pereira R. 2015a. Toxicity of solid residues  
696 resulting from wastewater treatment with nanomaterials. *Aquat. Toxicol.* 165, 172-178.  
697

698 Nogueira V., Lopes I., Rocha-Santos T. A. P., Rasteiro M. G., Abrantes N., Gonçalves F., Soares  
699 A.M.V.M., Duarte A.C., Pereira R., 2015b. Assessing the ecotoxicity of metal nano-oxides with  
700 potential for wastewater treatment. *Environ. Sci. Pollut. Res.* 22, 13212–13224.  
701

702 Nowack B., Ranville J.F., Diamond S., Gallego-Urrea, J.A., Metcalfe C., Rose J., Horne N.,  
703 Koelmans A.A., Klaine S.J. 2012. Potential scenarios for nanomaterial release and subsequent  
704 alteration in the environment. *Environ. Tox. Chem.* 31, 50-59.  
705

706 Nowack B., Baalousha, M., Bornhöft N., Chaudhry Q, Cornelis G., Cotterill J., Gondikas A.,  
707 Hassellöv M., Lead J., Mitrano D.M., von der Kammer F. and Wontner-Smith T., 2015. Progress  
708 towards the validation of modeled environmental concentrations of engineered nanomaterials by  
709 analytical measurements. *Env. Sci Nano* 2, 421-428.  
710

711 Otto M., Floyd M., Bajpai S. 2008. Nanotechnology for site remediation. *Remediation* 19, 99-108.  
712 Panzella L., Melone L., Pezzella A., Rossi B., Pastori N., Perfetti M., D’Errico G., Punta C.,  
713 d’Ischia M. 2016. Surface-functionalization of nanostructured cellulose aerogels by solid state  
714 eumelanin coating. *Biomacromol.* 17, 564-571.

715  
716 Patil S.S., Shedbalkar U.U., Truskewycz A., Chopade B.A., Ball A., 2016. Nanoparticles for  
717 environmental clean up: a review of potential risks and emerging solutions. *Env Technol Innov.*,  
718 5, 10-21.  
719  
720 PEN, The Project on Emerging Nanotechnologies. 2015. Nanoremediation Map. Available:  
721 [http://www.nanotechproject.org/inventories/remediation\\_map/](http://www.nanotechproject.org/inventories/remediation_map/)  
722  
723 Petersen Elijah J., Stephen A. Diamond, Alan J. Kennedy, Greg G. Goss, Kay Ho, Jamie Lead,  
724 Shannon K. Hanna, Nanna B. Hartmann, Kerstin Hund-Rinke, Brian Mader, Nicolas Manier,  
725 Pascal Pandard, Edward R. Salinas, and Phil Sayre. Adapting OECD Aquatic Toxicity Tests for  
726 Use with Manufactured Nanomaterials: Key Issues and Consensus Recommendations. *Environ.*  
727 *Sci. Technol.* 2015, 49, 9532–9547  
728  
729 Peijnenburg W., Praetorius A., Scott-Fordsmand J., Cornelis G. 2016. Fate assessment of  
730 engineered nanoparticles in solids dominated media – Current insights and the way forward.  
731 *Environ. Poll.* 218, 1365-1369.  
732  
733 Pierre G., Punta C., Delattre C., Melone L., Dubessay P., Fiorati A., Pastori N., Galante Y.M.,  
734 Michaud P. 2017. TEMPO-mediated oxidation of polysaccharides: An ongoing story. *Carbohydr.*  
735 *Polym.* 165, 71-85.  
736  
737 Praetorius A., Tufenkji N., Goss K.U., Scheringer M., von der Kammer F., Elimelech M. 2014. The  
738 road to nowhere: equilibrium partition coefficients for nanoparticles. *Environ. Sci. Nano.* 1, 317-  
739 323.  
740  
741 Qu X.L., Alvarez P.J., Li Q.L. 2013. Applications of nanotechnology in water and wastewater  
742 treatment. *Water Res.* 47, 3931–3946.  
743  
744 Semerad J., Cajthaml T. 2016. Ecotoxicity and environmental safety related to nano-scale  
745 zerovalent iron remediation applications. *Appl. Microbiol. Biotechnol.* 100, 9809-9819.  
746  
747 Setyono D., Valiyaveetil S. 2016. Functionalized paper - A readily accessible adsorbent for  
748 removal of dissolved heavy metal salts and nanoparticles from water. *J. Hazard. Mat.* 302, 120-  
749 128.  
750  
751 Shao T., Zhang P., Li Z., Jin L. 2013. Photocatalytic decomposition of perfluorooctanoic acid in  
752 pure water and wastewater by needle like nanostructured gallium oxide. *Chin. J. Catal.* 34, 1551–  
753 1559.  
754  
755 Sheehana C. and Harrington J. 2012. An environmental and economic analysis for geotube coastal  
756 structures retaining dredge material. *Res. Cons. Recycl.* 61, 91–102.  
757  
758 SiCon, 2016. “Contaminated sites. Experiences in remediation activities.”, 11-13 February 2016,  
759 Brescia, Italy.  
760  
761 Stone V., Nowack B., Baun A., van den Brink N., von der Kammer F., Dusinska M., Handy R.,  
762 Hankin S, Hasselov M., Joner E. Fernandes T.F. 2010. Nanomaterials for environmental studies:

763 Classification, reference material issues, and strategies for physico-chemical characterization. *Sci.*  
764 *Tot. Environ.* 408, 1745-1754.

765

766 SuRF Italy (2014). *Sostenibilità nelle bonifiche in Italia. Libro bianco 2014*, pp. 108.

767

768 Tiraferri A., Saldarriaga Hernandez, L.A., Bianco C., Tosco T., Sethi R. 2017. Colloidal behavior of  
769 goethite nanoparticles modified with humic acid and implications for aquifer reclamation. *J. Nano.*  
770 *Res.* in press.

771

772 Tosco T., Petrangeli Papini M., Cruz Viggi C., Sethi R. 2014a. Nanoscale iron particles for  
773 groundwater remediation: a review. *J. Clean. Prod.* 77, 10-21.

774

775 Tosco, T., Gastone, F., Sethi, R. 2014b. Guar gum solutions for improved delivery of iron particles  
776 in porous media (Part 2): Iron transport tests and modeling in radial geometry. *J. Contam. Hydr.*  
777 166, 34-51.

778

779 Trujillo-Reyes J., Peralta-Videa J.R., Gardea-Torresdey J.L. 2014. Supported and unsupported  
780 nanomaterials for water and soil remediation: Are they a useful solution for worldwide pollution?  
781 *J. Hazard. Mat.* 280, 487-503.

782

783 US Environmental Protection Agency (USEPA). 2004 *Cleaning up the Nation's waste sites:*  
784 *Markets and technology trends*, EPA 542-R-04-015,. Washington, DC: US Environmental  
785 Protection Agency.

786

787 US Environmental Protection Agency (USEPA). 2009. National priorities list (NPL). Available:  
788 <http://www.epa.gov/superfund/sites/npl/>

789

790 US Environmental Protection Agency (USEPA). 2013. *Remediation Technologies*. Available:  
791 <http://www.epa.gov/superfund/remedytech/remed.htm>

792

793 Wang C.B., Zhang W.X. 1997. Synthesizing nanoscale iron particles for rapid and complete  
794 dechlorination of TCE and PCBs. *Environ. Sci. Techn.* 31, 2154-2156.

795

796 Zhou C., Vitiello V., Casals E., Puntès V.F., Iamunno F., Pellegrini D., Changwen W., Benvenuto  
797 G., Buttino I. 2016. Toxicity of nickel in the marine calanoid copepod *Acartia tonsa*: Nickel  
798 chloride versus nanoparticles. *Aquat. Toxicol.* 170, 1-12.

Table 1. List of the most commonly successfully used ENMs for groundwater, water and wastewater remediation for which ecotoxicity<sup>§</sup> has been reported (List of ENMs and their applications adapted from Patil et al., 2016).

ENMs	Contaminants in environmental media			Ecotoxicity	References
	Groundwater	Water	Wastewater		
<b>nZVI</b>	Chlorinated compounds (PCE, TCE, DCE) Heavy metals (Pd, Cr, Cu, As, Cr, Zn)	As Phenol	Organic pollutants (PCP, 2,4 DCP) Heavy metals (U, Cr, Ni, Cu, Pb)	Marine organisms (bacteria, algae, invertebrates)	Kadar et al., 2012
<b>TiO<sub>2</sub></b>		Organic pollutants (TCP, 2,4-DCP, benzene) Nitrates, NOM, liological contaminants, Cr		Marine and freshwater organisms (bacteria, algae, invertebrates, marine mammals)	Baun et al., 2008 Minetto et al., 2016 Ma et al., 2013
<b>ZnO</b>		Explosive compounds Phenanthrene			
<b>Ag/Fe Ni/Fe Cu/Fe</b>	Hexachlorobenzene				
<b>Carbon nanotubes</b>		NOM, toxins and pathogens	Organic pollutants (pesticides, pharmaceuticals)	Marine and freshwater organisms (bacteria, invertebrates, fish)	Baun et al., 2008 Minetto et al., 2016

<sup>§</sup>Ecotoxicity data are referred to bare particles and cannot be generalized to the diversity of specific particles used in remediation.

PCE (Tetrachloroethylene); TCE (Trichloroethylene); DCE (1,2-dichloroethane); TCP (tetrachlorophenol); 2,4 DCP (2,4-diclorophenol); NOM (natural organic matter)

# Sustainable and ecosafe nanoremediation

*A way forward to overcome current limitations*

