

# Nanotechnologies for environmental cleanup

Among the many applications of nanotechnology that have environmental implications, remediation of contaminated groundwater using nanoparticles containing zero-valent iron (nZVI) is one of the most prominent examples of a rapidly emerging technology with considerable potential benefits. There are, however, many uncertainties regarding the fundamental features of this technology, which have made it difficult to engineer applications for optimal performance or to assess the risk to human or ecological health.

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In this review, we address three of the fundamental features commonly contributing to a misunderstanding of this technology showing that: (i) the nZVI used in groundwater remediation is larger than particles that exhibit 'true' nanosize effects; (ii) the higher reactivity of this nZVI is mainly the result of its high specific surface area; and (iii) the mobility of nZVI will be less than a few meters under almost all relevant conditions. One implication of its limited mobility is that human exposure resulting from remediation applications of nZVI is likely to be minimal. There are, however, many characteristics of this technology about which very little is known: e.g. how quickly nZVI will be transformed and to what products, whether this residue will be detectable in the environment, and how surface modifications of nZVI will alter its long-term environmental fate and effectiveness for remediation.

Among the numerous promising applications of nanotechnology, there are many that involve the environment. This is reflected in the

selection of 'environmental improvement' as one of eight cross-cutting areas of nanotechnology applications identified by the US National Nanotechnology Initiative (NNI)<sup>1</sup>. In fact, almost all of the NNI's seven program component areas (fundamental phenomena, materials, devices, metrology, etc.) have environmental aspects, and environmental concerns figure in the missions of almost all 11 US Federal agencies that participate in the NNI<sup>1,2</sup>.

Most environmental applications of nanotechnology fall into three categories: (i) environmentally-benign and/or sustainable products (e.g. green chemistry or pollution prevention), (ii) remediation of materials contaminated with hazardous substances, and (iii) sensors for environmental agents<sup>3,4</sup>. Although these three categories are usually construed in terms of chemical substances or nonbiological materials, it should be noted that they also apply to microbial agents and biological materials. In particular, nanotechnologies play a large role in current efforts to develop better methods for detection and decontamination of

harmful biological agents<sup>5</sup>, which are – in many respects – environmental issues.

With respect to remediation of environmental contaminants, the range of nanotechnology applications mirrors the spectrum of 'non-nano' strategies for contaminant remediation. Two of the major distinctions that define types of conventional remediation technologies also apply to nanotechnologies for remediation: adsorptive versus reactive and *in situ* versus *ex situ*. Adsorptive remediation technologies remove contaminants (especially metals) by sequestration, whereas reactive technologies affect degradation of contaminants, sometimes all the way to harmless products (e.g. CO<sub>2</sub> and H<sub>2</sub>O in the case of organic contaminants). *In situ* technologies involve treatment of contaminants in place, whereas *ex situ* refers to treatment after removing the contaminated material to a more convenient location (e.g. pumping contaminated groundwater to the surface and treatment in above-ground reactors).

### Ex situ nanotechnology

A prominent example of a nanotechnology for contaminant remediation by adsorption is known as self-assembled monolayers on mesoporous supports (SAMMS)<sup>6</sup>. SAMMS are created by self-assembly of a monolayer of functionalized surfactants onto mesoporous ceramic supports, resulting in very high surface areas (~1000 m<sup>2</sup>/g) with adsorptive properties that can be tuned to target contaminants such as mercury, chromate, arsenate, pertechnetate, and selenite. Dendritic polymers are another type of nanostructured material that has the potential for use in remediation. Recent examples of this approach include dendrimer-enhanced ultrafiltration to remove Cu(II) from water<sup>7</sup> and soil washing to remove Pb(II) contamination<sup>8</sup>. Both of these types of nanostructured adsorbents are most likely to be applied *ex situ*, where they can be recovered with the concentrated hazardous material that they adsorb.

Nanotechnologies that affect remediation by contaminant degradation – rather than adsorption – are particularly attractive for organic contaminants. A well-established approach for remediation of organic contaminants is photooxidation catalyzed by semiconductors such as TiO<sub>2</sub><sup>9</sup>, and the potential benefits of quantum-sized (< ~10 nm) photocatalysts have long been recognized for contaminant degradation applications<sup>10-12</sup>. However, as with the adsorptive technologies described above, photooxidation with nanostructured semiconductors is primarily an *ex situ* strategy, in this case because effective illumination usually requires that treatment be done in a reactor that is designed for this purpose.

### In situ nanotechnology

*In situ* degradation of contaminants, when feasible, is often preferred over other approaches because it has the potential to be more cost effective. However, *in situ* remediation requires delivery of the treatment to the contamination and this has proven to be a major

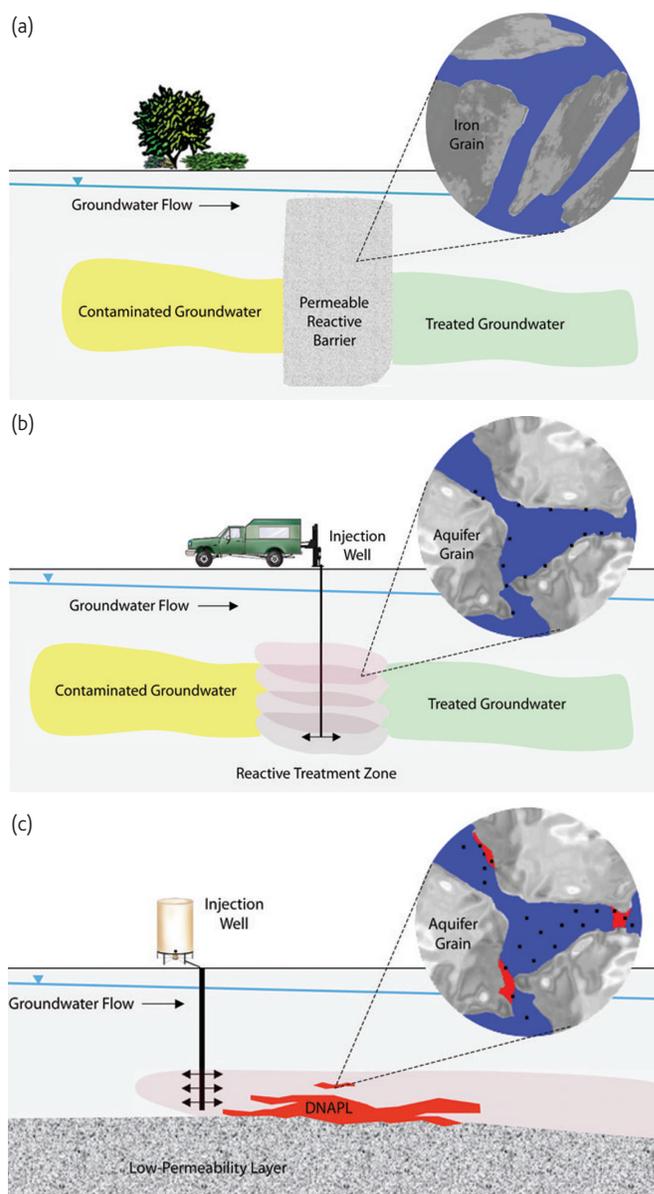


Fig. 1 Three approaches to application of Fe particles for groundwater remediation: (a) a conventional 'permeable reactive barrier' made with millimeter-sized construction-grade granular Fe; (b) a 'reactive treatment zone' formed by sequential injection of nanosized Fe to form overlapping zones of particles adsorbed to the grains of native aquifer material; and (c) treatment of nonaqueous phase liquid (DNAPL) contamination by injection of mobile nanoparticles. In (b) and (c), nanoparticles are represented by black dots and zones that are affected by nanoparticles are represented as pink plumes. In (b), the nanoparticles are assumed to have little mobility in the porous medium; whereas in (c), nanoparticles modified to impart significant mobility are necessary. Note that reaction will only occur when contaminant – either dissolved in the groundwater or as DNAPL – comes into contact with the Fe surfaces.

obstacle to expanded development of *in situ* remediation technologies. With respect to this issue, nanotechnology has special relevance because of the potential for injecting nanosized (reactive or adsorptive) particles into contaminated porous media such as soils, sediments, and

aquifers. In this manner, it should be possible to create either: (i) *in situ* reactive zones with nanoparticles that are relatively immobile; or (ii) reactive nanoparticle plumes that migrate to contaminated zones if the nanoparticles are sufficiently mobile (as shown in Fig. 1). The *in situ* mobility of nanoparticles will be discussed further below, because it is a common source of misunderstanding.

Although a variety of types of nanoparticle might be applicable to *in situ* remediation (e.g. nonionic amphiphilic polyurethane<sup>13</sup> or alumina-supported noble metals<sup>14</sup>), by far the greatest interest is currently in nanoparticles that contain nZVI. The appeal of nZVI for remediation stems from the potential for improved remediation chemistry and/or expanded options for deployment<sup>15</sup> that complement the already well-developed science<sup>16</sup> and engineering<sup>17</sup> of contaminant remediation with millimeter-sized 'conventional' ZVI. This combination of factors has led to very rapid transfer of this technology from preliminary laboratory testing<sup>18</sup> to pilot-scale demonstrations in the field<sup>19</sup>. Full-scale commercial applications of nZVI in remediation are quickly becoming common, and there already are competitive markets among purveyors of nZVI materials and geotechnical service providers with various methods for deploying nZVI.

The rapid emergence of remediation technologies based on nZVI has obscured – and perhaps even exacerbated – some pervasive misconceptions regarding the fundamental principles underlying this technology and the practical implications of its use in the environment. Even though the issues are highly interrelated, we can group them into three categories: particle morphology, reactivity, and mobility. A few key considerations from each category are highlighted below with the hope of contributing to a consensus understanding regarding this nanotechnology, which might also help in future development of other nanotechnologies for environmental improvement.

## Nanoparticle characteristics

### Morphology

Various definitions have been given for 'nanosize', but most invoke (or imply) the notion that there is a size regime between that of molecules and materials where particles have properties that are unique, or at least qualitatively different than those of larger particles. The most compelling examples of such properties arise only for particles smaller than ~10 nm, where particle size approaches the length-scale of certain molecular properties<sup>20</sup>. One such example is that of quantum confinement, which arises because the bandgap increases as particle size decreases, and this effect contributes to some of the useful properties of nanosized semiconductor photocatalysts, as discussed above under *ex situ* nanotechnologies.

Another property that changes dramatically below 10 nm is specific surface area, as shown in Fig. 2. Qualitatively similar trends apply to related properties such as the ratio of surface/bulk atoms<sup>20</sup> and the fraction of particle volume comprised by a surface layer of finite thickness<sup>21</sup>. While trends such as these exhibit 'edges' that fall

around 10 nm (e.g. Fig. 2), the curves extend continuously to larger particle sizes. It is in this region – between 10s and 100s of nanometers – where we find the preparations of nZVI that are currently used in remediation applications<sup>22,23</sup>. Furthermore, even under laboratory conditions, particles of nZVI tend to aggregate, producing clusters that may approach microns in size<sup>24</sup>. These considerations suggest that nZVI, and related materials that are used in environmental remediation applications, will not exhibit the extraordinary properties that apply to 'true' nanosized particles, and will behave in most respects like environmental colloids, which have been studied extensively for decades<sup>25</sup>.

### Reactivity

The greater reactivity that is often ascribed to nanoparticles can be the result of larger overall surface area, greater density of reactive sites on the particle surfaces, and/or higher intrinsic reactivity of the reactive surface sites. Together, these factors have produced three operationally distinct results for nZVI: (i) degradation of contaminants that do not react detectably with larger particles of similar material (e.g. polychlorinated biphenyls<sup>26</sup>); (ii) more rapid degradation of contaminants that already react at useful rates with larger particles (e.g. chlorinated ethylenes<sup>23,27</sup>); or (iii) more favorable products from contaminants that are rapidly degraded by larger materials but that yield undesirable byproducts (e.g. carbon tetrachloride<sup>22</sup>).

Of these three types of reactivity effects, the second (faster degradation of already degradable contaminants) is noted most frequently. The cause of this effect, however, is rarely identified, even though the question has practical, as well as fundamental, significance. To investigate this question, we compared surface-area normalized rate constants ( $k_{sa}$ ) against mass normalized rate constants ( $k_m$ ) for the degradation of carbon tetrachloride by ZVI (Fig. 3). The results show

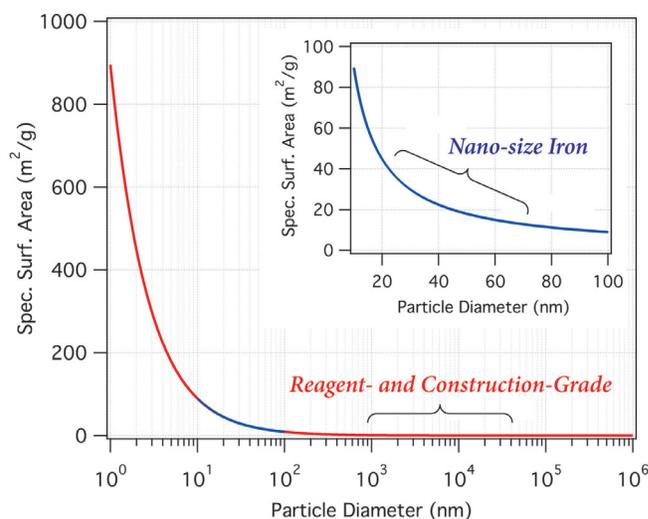


Fig. 2 Particle surface area calculated from diameter assuming spherical geometry and density  $6.7 \text{ g/cm}^3$  (based on the average of densities for pure  $\text{Fe}^0$  and  $\text{Fe}_3\text{O}_4$ ).

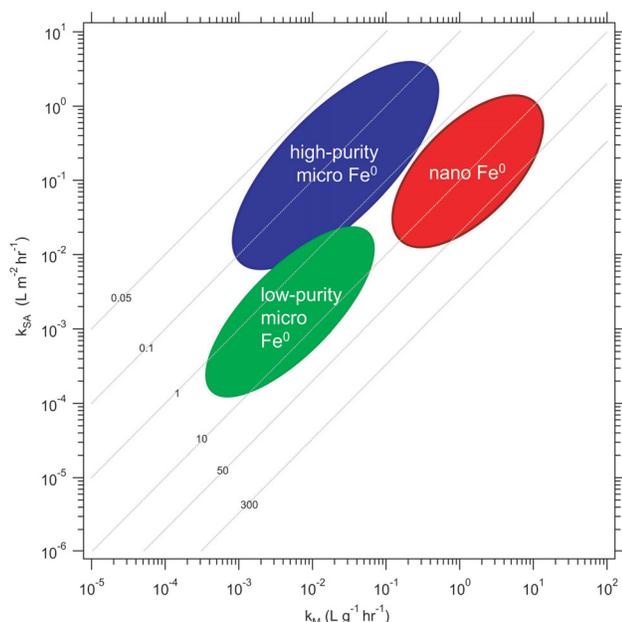


Fig. 3 Comparison of rate constants for reduction of  $\text{CCl}_4$  by nZVI and two types of millimeter-sized  $\text{Fe}^0$ . Ovals are based on ~50 data compiled from a variety of sources. A precursor to this figure was published by Nurmi et al.<sup>22</sup>.

that nZVI gives larger  $k_m$  but similar  $k_{sa}$  values when compared with millimeter-sized ZVI, suggesting that the higher rate of carbon tetrachloride degradation by nZVI is the result of its high surface area and not the greater abundance of reactive sites on the surface or the greater intrinsic reactivity of surface sites<sup>22</sup>. This conclusion may hold for other contaminants reacting with nZVI under conditions relevant to environmental remediation, but the available data are inconclusive. Note, however, that this analysis does not include data for bimetallic combinations of nZVI with noble metal catalysts like Pd, Ni, or Cu. These bimetallic materials generally do give larger values of  $k_{sa}$ , but the enhancement is primarily the result of the catalytic effect of the noble metals, which is also observed with larger particles<sup>28</sup>.

Regardless of the precise reason for high reactivity, high reactivity tends to correlate with low selectivity, which makes remediation with nZVI susceptible to inefficiency because of the reaction of the particles with nontarget substances, including dissolved oxygen and water<sup>23</sup>. This 'natural demand', together with the demand arising from the reaction with the target contaminants, implies that nZVI will have a limited lifetime in environmental porous media, potentially necessitating reinjections of nZVI and thereby adding to the cost of treatment<sup>29</sup>. Alternatively, a short lifetime of nZVI *in situ* could prove to be beneficial by limiting the potential for unwanted exposure at receptors down-gradient (if the particles exhibit significant mobility).

### Mobility

It is commonly assumed that nanoparticles will be highly mobile in porous media because they are much smaller than the relevant pore spaces, but this is an oversimplification. In general, the mobility of

nanoparticles in saturated environmental porous media is determined by the product of the number of nanoparticle collisions with the porous medium per unit transport distance and the probability that any collision will result in removal of the nanoparticle from the flow system (i.e. the sticking coefficient)<sup>30</sup>. Collisions may result from three processes: Brownian diffusion, interception, and gravitational sedimentation.

For nanoparticles, under conditions that are typical of environmental porous media, Brownian diffusion is the dominant collision process<sup>30,31</sup>. For particles greater than ~400 nm and with high densities (e.g. 7.68 g/cm<sup>3</sup> for pure  $\text{Fe}^0$  particles), gravity effects can become important. Using the single-collector efficiency approach presented by Tufenkji and Elimelech<sup>30</sup> and deep-bed filtration theory, it is possible to calculate the transport distance over which 99% removal of nanoparticles would occur as a function of subsurface characteristics and the sticking coefficient. Fig. 4 shows that for typical subsurface conditions, transport distances range from millimeters to a few tens of meters depending on the sticking coefficient. Reported sticking coefficients<sup>32</sup> for unmodified nZVI in several types of porous media range from 0.14 to ~1, which translates to transport distances of only a few centimeters in porous media under typical groundwater conditions (Fig. 4). This has led to considerable interest in surface modification of nanoparticles to increase transport distances<sup>32,33</sup>. Smaller sticking coefficients for these and other nanoparticles have been reported (0.01 for surface-treated Fe nanoparticles<sup>32</sup> and 0.0001 for carbon-based nanoparticles<sup>34</sup>), but even these low sticking coefficients do not predict mobility in groundwater for more than a few meters, except at very high groundwater velocities and possibly in fractures.

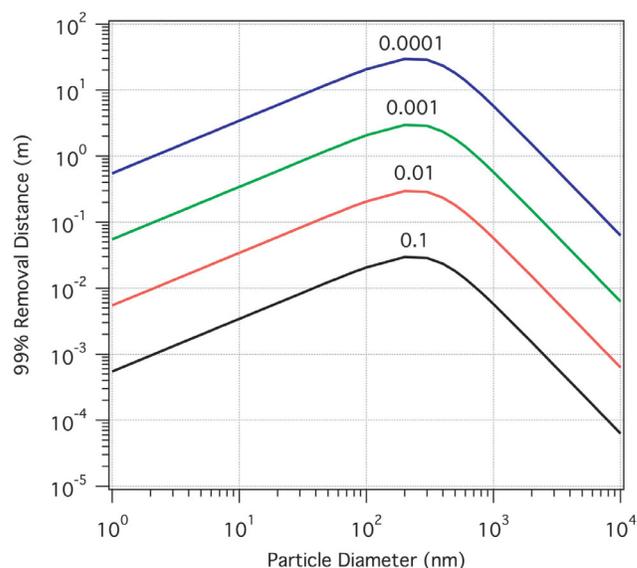


Fig. 4 Calculated distance over which 99% of the nanoparticles are removed for sticking coefficients 0.1, 0.01, 0.001, and 0.0001. Assumed subsurface conditions include: porosity = 0.36, velocity = 0.1 m/day, soil particle diameter = 0.3 mm, nanoparticle density = 6.7 g/cm<sup>3</sup>.

## Risks

The above discussion of the morphology, reactivity, and mobility of nanoparticles in the context of environmental remediation demonstrates that our current understanding of the basic processes involved in this technology is still evolving and incomplete. In addition to making it difficult to move forward with the engineering of full-scale implementations, these uncertainties make it very difficult to assess the risks that this technology might have to human or ecological health<sup>35</sup>. Specifically with respect to *in situ* applications of nZVI (or related materials) to remediation of environmental porous media, there is not yet any research and development that directly and substantively addresses the issue of risk. Recognizing this, some groups have adopted the 'precautionary' position that *in situ* applications of nanoparticles for remediation should be prohibited<sup>36</sup>, whereas others have recommended, in effect, that research on all fronts should proceed in parallel<sup>37</sup>.

This dilemma of how (or whether) to regulate the application of nanoparticles to remediation should be alleviated soon, as the results from on-going studies become available<sup>38</sup>. Until then, risk assessment

regarding *in situ* applications of nanoparticles in remediation will continue to be based largely on extrapolations from considerations developed from studies of related, but potentially quite different, contexts where nanoparticles occur in the environment. Foremost among these are the inhalation of 'ultrafine' airborne particles, on which there is an extensive literature<sup>39</sup>, and the toxicology of carbon-based nanoparticles such as fullerenes and nanotubes, on which a literature is rapidly taking shape<sup>35</sup>. At this time, however, we can conclude that nZVI and the related materials used for *in situ* remediation applications are not as small, reactive, persistent, or mobile as most of the materials for which specific evidence is available suggesting the potential for human or ecological risk. [nl](#)

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## REFERENCES

- Nanoscale Science, Engineering, and Technology Subcommittee, Committee on Technology, National Science and Technology Council, *The National Nanotechnology Initiative Strategic Plan* (2004)
- Nanoscale Science, Engineering, and Technology Subcommittee, Committee on Technology, National Science and Technology Council, *The National Nanotechnology Initiative Strategic Plan, Supplement to the President's 2006 Budget* (2005)
- Masciangioli, T., and Zhang, W.-X., *Environ. Sci. Technol.* (2003) **37**, 102A
- Karn, B., et al., (eds.), *Nanotechnology and the Environment: Applications and Implications*, Oxford University Press, Oxford UK (2005)
- Koper, O. B., et al., *Curr. Microbiol.* (2002) **44**, 49
- Fryxell, G. E., et al., In *Encyclopedia of Nanoscience and Nanotechnology*, Dekker, New York, NY (2004), 1125
- Diallo, M. S., et al., *Environ. Sci. Technol.* (2005) **39**, 1366
- Xu, Y., and Zhao, D., *Ind. Eng. Chem. Res.* (2006) **45**, 1758
- Hoffmann, M. R., et al., *Chem. Rev.* (1995) **95**, 69
- Obare, S. O., and Meyer, G. J., *J. Environ. Sci. Health* (2004) **A39**, 2549
- Abrams, B., and Wilcoxon, J., *Crit. Rev. Solid State Mater. Sci.* (2005) **30**, 153
- Kamat, P. V., and Meisel, D., *Comptes Rendus Chimie* (2003) **6**, 999
- Tungittiplakorn, W., et al., *Environ. Sci. Technol.* (2005) **39**, 1354
- Nutt, M. O., et al., *Environ. Sci. Technol.* (2005) **39**, 1346
- Zhang, W., *J. Nanoparticle Res.* (2003) **5**, 323
- Tratnyek, P. G., et al., In *Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications*, Marcel Dekker, New York, NY (2003), 371
- Interstate Technology and Regulatory Council (ITRC), *Permeable Reactive Barriers: Lessons Learned/New Directions*, ITRC (2005)
- Wang, C. B., and Zhang, W. X., *Environ. Sci. Technol.* (1997) **31**, 2154
- Elliott, D. W., and Zhang, W. X., *Environ. Sci. Technol.* (2002) **35**, 4922
- Klabunde, K. J., et al., *J. Phys. Chem.* (1996) **100**, 12142
- Navrotsky, A., In *Encyclopedia of Nanoscience and Nanotechnology*, Marcel Dekker, New York, NY (2004), 1147
- Nurmi, J. T., et al., *Environ. Sci. Technol.* (2005) **39**, 1221
- Liu, Y., et al., *Environ. Sci. Technol.* (2005) **39**, 1338
- Saleh, N. B., et al., *Preprints of Extended Abstracts, 230<sup>th</sup> ACS National Meeting, Washington, DC, Aug. 28-Sept. 1, 2005*, American Chemical Society, Division of Environmental Chemistry (2005) **45**, 703
- Ryan, J. N., and Elimelech, M., *Colloids Surf.* (1996) **A107**, 1
- Lowry, G. V., and Johnson, K. M., *Environ. Sci. Technol.* (2004) **38**, 5208
- Song, H., and Carraway, E. R., *Environ. Sci. Technol.* (2005) **39**, 6237
- Muftikian, R., et al., *Water Res.* (1995) **29**, 2434
- Gillham, R. W., *Ground Water Monitor. Remed.* (2003) **23**, 6
- Tufenkji, N., and Elimelech, M., *Environ. Sci. Technol.* (2004) **38**, 529
- Logan, B. E., *Environmental Transport Processes*, John Wiley & Sons, New York, NY (1999)
- Schrick, B., et al., *Chem. Mater.* (2004) **16**, 2187
- Saleh, N., et al., *Nano Lett.* (2005) **5**, 2489
- Lecoanet, H. N., et al., *Environ. Sci. Technol.* (2004) **38**, 5164
- Colvin, V. L., *Nat. Biotechnol.* (2003) **21**, 1166
- The Royal Society and The Royal Academy of Engineering, *Nanoscience and Nanotechnologies: Opportunities and Uncertainties*, The Royal Society and The Royal Academy of Engineering, London UK (2004)
- Nanotechnology Workgroup, Science Policy Council, US Environmental Protection Agency, *Nanotechnology White Paper* (2005).
- Dunphy Guzman, K. A., et al., *Environ. Sci. Technol.* (2006) **40**, 1401
- Oberdörster, G., et al., *Environ. Health Perspect.* (2005) **113**, 823