The Use of Nanoscale Zero Valent Iron for Environmental Remediation – Benefits and Possible Pitfalls

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ABSTRACT

Nanoscale zero valent iron (nZVI) is the primary nanoscale particle (NP) that is being used to remediate contaminated sites. Golder Associates Ltd./Inc. has used nZVI for remediation of trichloroetheylene contaminated sites in various pilot and field scale studies. In situ remediation using nZVI has achieved significant reductions of contaminants in relatively short periods of time. The results from several pilot and full-scale tests from industrial sites throughout Canada and the United States will be discussed.

Knowledge on the impact of NPs to the environment and human health is still very incipient. Therefore, in addition to developing new nanotechnology tools for remediation we are also cognizant of the parallel requirements of safeguarding human health and the environment. To address the potential environmental impact of using nZVI, Golder/HydroQual have been actively investigating the effects of environmental exposure to NP for various aquatic and terrestrial receptors using accepted standard methods. Barley, earthworms and soil microbes were used as representative terrestrial organisms and *Hyallela Azteca* (Freshwater Amphipods) and Chironomids as aquatic sediment organisms to examine exposure effects. Results from these studies will be discussed in this paper.

Keywords: nanoscale zero valent iron, remediation

1 INTRODUCTION

Nanotechnology is a rapidly emerging science that not only has the potential to impact every facet of the science and technology, but our daily lives. According to the National Nanotechnology Initiative, nanotechnology is defined as the "understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications…Unique physical, chemical and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules". Interest in using nanotechnology is strongly associated with the unique physical, chemical and biological properties of these particles observed in the nanoscale. Also, because nanoscale particles are engineered and highly tunable, coatings and surfaces can be tailored to have specific functions or characteristics.

For these reasons, the use of nanoscale particles is particularly attractive for environmental remediation purposes. In the 1980's the signing of the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) or Superfund, enabled the US Environmental Protection Agency (USEPA) to compel parties responsible to remediate contaminated sites. In situations where responsible parties could not be identified, the Agency would clean up the site using a special trust fund (USEPA). Within the Superfund Program is a National Priorities List (NPL) where the most contaminated sites are classified. As of 2009, there are 1255 sites on the NPL. It is estimated that it will take between 30 – 35 years for these site to be remediated, at a cost of $250 billion USD [1] using conventional technologies (e.g. dig and dump). To expedite the recovery of Superfund sites, in 2009, the American Recovery & Reinvestment Act infused 2.3 billion USD for environmental clean up, of which 800 million USD was allocated for the superfund sites specifically listed on the NPL [3].

In addition to staggering cost estimates, the amount of time that is required to remediate these sites is often fairly lengthy. These outlined time and cost estimates increase the appeal of using nanotechnology as an alternative to conventional remediation technologies. Due to their small size, nanoscale particles offer a significant increase in specific surface area (SSA), leading to greater area for surface reactivity and a faster reaction rate. For example, comparing SSA of micro ZVI to nano ZVI, the SSA increases from 10 m^2/Kg to 30,000 m^2/Kg. Although the actual cost of production for nanoscale particles is significantly higher, this difference is mitigated by the large increase in SSA, which translates into fewer particles required to achieve the desired effects. Furthermore, due to their size, nanoscale particles should be able to move further into smaller subsurface spaces. There are some estimates that demonstrate a 10 fold decrease in costs when nanotechnology is used as compared to conventional dump and treat technologies [1].

Currently, nanoscale zero valent iron (nZVI) is the nanoscale particle that is primarily being used for remediation. Golder has implemented nZVI in many successful pilot-scale and field-scale studies to clean up sites contaminated by chlorinated compounds and heavy metals. Results from several pilot studies will be discussed. In addition to using nZVI for environmental clean up, HydroQual (a wholly owned subsidiary of Golder Associates) is actively involved in determining whether nanoscale particle exposure poses a threat to the environment and how to accurately measure these effects. The use of nanoscale particles in the field and the field-based environmental exposure effects will also be discussed in this paper.

2 NANOSCALE ZERO VALENT IRON – LABORATORY STUDIES AND FIELD IMPLEMENTATION

Nanoscale zero valent iron can be produced through a top down grinding process or a bottom up chemical synthesis process. Golder Associates is licensed by Lehigh University since 2005 to produce nZVI via the top down grinding method, to be applied for environmental remediation. Nanoscale zero valent iron is very effective at reducing halogenated hydrocarbons to benign hydrocarbons and can also transform sites contaminated with metal ions, heavy metal ions and radionuclides [2] through various mechanisms including adsorption and precipitation. The degradation of chlorinated volatile organic carbons by nZVI occurs through a β-elimination or hydrogenolysis pathway.

In laboratory scale studies, rapid and complete dechlorination of all chlorinated compounds was observed within water and soil-water slurries. In batch reactors with only nZVI, a 99% reduction in contaminants [TCA (trichloroethane), TCE (trichloroethylene) and PCE (tetrachloroethylene)] was achieved in 24 hours while decontamination in treatments containing both nZVI and palladium added as a catalyst, achieved levels below detection limits within 8 hours. This author further suggests that nZVI will remain active within soil and water environments for periods of time ranging from 6-8 weeks [2].

Golder Associates Ltd., Golder Associates Inc. and Golder Associates GMBH have successfully used nZVI in several pilot and field scale studies in Canada, the United States and Germany, respectively. The efficacy of nZVI for remediation of contaminated sites has been successfully employed in a variety of geological media, including porous and bedrock media. nZVI is introduced into the ground via direct push or gravity/pressure injection methods in the form of a slurry where fresh nZVI is mixed with potable water, a food grade surface modifier to enhance deliverability and palladium as a catalyst.

In North Carolina, in a pilot test implemented by Golder Associates, Inc. in conjunction with Lehigh University, approximately 11 kg of nZVI/Pd (BNP; slurry injection, total volume 6056 L) was injected into bedrock by gravity injection. Initial measurements taken at the site showed the key contaminants of concern were TCE, DCE, PCE, and VC (vinyl chloride). The pre-injection concentrations of TCE were 14000 ug/L and ORP values of +400 mV. After nZVI was injected into the bedrock there was a greater than 90% reduction in pre-injection levels of TCE, while DCE levels decreased to concentrations below that of groundwater quality standards. The ORP also decreased from pre-injection levels to -400 to -500 mV, introducing favorable reducing conditions to the site.

In 2006, Golder Associates GMBH used nZVI to treat a contaminated industrial site in Germany. The key contaminants of concern at this site were chlorinated hydrocarbons (CHC; 50 000 ug/L pre injection concentration), chromium (1000 ug/L pre-injection concentration) and nickel (2000 ug/L pre injection concentration). One hundred and twenty kilograms of nZVI in the form of a slurry were introduced into porous unconsolidated sediment via pressure injection. At observation wells 2 months post injection, CHC levels decreased by 10% of initial concentrations and heavy metals levels decreased to below analytical detection limits.

In Canada, Golder Associates Ltd. used nZVI to treat a site in Quebec where there was a 4 km plume of contamination with the key contaminants being TCE, DCE and traces of VC. Similar to the other sites discussed, 4000 kg of nZVI in the form of a slurry were introduced into the site using pressure injection. After 1 month of treatment TCE concentrations decreased by 50-60% of post injection values and a greater than 80% reduction was achieved 1 month post injection (Figure 1).

The remediation of contaminated sites using nZVI has met with fairly high level of success; however, there are limitations to its capabilities. The success of nZVI is highly dependent on the geology, hydrogeology, geochemistry and microbiology of the site. These parameters must be thoroughly assessed prior to implementation of nZVI for remediation.

3 TOXICITY TESTING

A key challenge facing any new technology is the understanding of the potential long-term environmental impacts of exposure. In particular for nanotechnology, since by definition the particles may have physical, chemical and biological properties and reactivity (due to their small size) that differ from the bulk counterpart, responding to this challenge is paramount. The inherent nature of these particles implies the need to examine whether exposure to these particles may produce a toxicological profile that is different from the bulk counterparts. To address the potential environmental impact of using nZVI, HydroQual has been actively investigating the consequences of environmental exposure to nanoscale particles for various aquatic and terrestrial receptors using accepted standard methods. For this particular study, barley, earthworms and soil microbes were used as representative terrestrial organisms and *Hyallela Azteca* (Freshwater Amphipods) and Chironomids were used as aquatic sediment organisms to examine exposure effects. In this section, we describe nZVI and the test methods used to assess hazard.

3.1 Nanoscale Zero Valent Iron

Nanoscale zero valent iron used for experimental testing was manufactured by Golder Associates Inc. The slurry produced for testing is the same formulation as used in field scale applications (proprietary).

3.2 Experimental Testing

Acute and sublethal exposure effects were measured using standard Environment Canada methods. For terrestrial testing EPS 1/RM/45 was followed to measure exposure effects to barley [4] and EPS 1/RM/43 was followed for earthworms [5]. For aquatic testing we used EPS 1/RM/33 for *Hyalella* [6] and for Chironomids [7] we followed EPS 1/RM/32.

To measure changes in soil microbial profiles, artificial soil [artificial soil (1:2:7 ratio): peat moss, Koalinite clay, silica sand] samples spiked with nZVI and ZVI were taken on Day 3 and Day 14 after treatments. These samples were tested using DNA profiling techniques.

All treatments were run at 100% field sample concentrations, 50% and 25%. Nanoscale zero valent iron exposure effects were compared to the parent material from which nZVI produced (BASF ZVI 200; BASF Corporation, Florham, New Jersey). Control samples included DRO water as the negative control, food grade surface modifier and palladium as background controls.

3.3 Statistical Analysis

Statistical analysis (ANOVA, Post Hoc analysis student T-test) was performed on test samples using PAST® and JMP® software.

4 RESULTS AND DISCUSSION

Nanotechnology is a rapidly emerging field that has the potential to impact virtually all aspects of science, including new remediation technologies. The use of nZVI for remediation of industrial waste sites is rapidly moving from pilot scale to full scale field studies where large amounts of iron will be introduced into the environment. It is very promising that pilot scale studies demonstrate the efficacy of nZVI for decontaminating chlorinated compounds and heavy metals. As we are moving towards full scale implementation of nZVI, the amount of iron that will be introduced into the environment will significantly increase. This emphasizes the need to understand whether there is a major environmental impact of exposing organisms to nZVI. This study was done to determine whether exposure effects to nZVI differed from that of its bulk parent material at field applied concentrations.

In this study exposure of terrestrial organisms to both nanoscale and bulk scale iron did not produce any significant acute or sublethal exposure effects, with the exception of shoot length and biomass (Table 1). As compared to the negative control, exposure to both nanoscale and bulk iron samples induced significant growth effects on shoot length and biomass. Since similar exposure effects were observed in both the nano and bulk scale, decreases in shoot length and biomass cannot be attributed to nano-specific exposure. Although exposure effects were not size specific the impact of the amount of nZVI that will be introduced into the ground and as a consequence the surrounding environment may have potential impacts on the growth of vegetation in and around the area of remedial action.

In the aquatic tests performed, similarly to the terrestrial tests, exposure to nanoscale and bulk scale iron at the concentrations tested seemed innocuous to sediment dwelling organisms, as survival was not significantly impacted. There was neither acute nor sublethal exposure effects observed.

The final test that we performed was to evaluate the impact of nZVI and ZVI exposure on microbial populations present in artificial soil. Comparisons were made between day 3 and day 14 results of DNA "fingerprint" patterns of treated soils (Figure 2). There was a general increase in bacterial diversity for nZVI and ZVI samples by day 14 as compared to day 3 and controls as seen with an increase in the number of bands present. The amount of particles added to the soil influenced the number of bands (diversity) and/or intensity of single bands (faint × darker), indicating a dose response. Also, nZVI and ZVI sample band patterns were similar at day 3, with the exception of noticeable differences in band intensity on nZVI-100. At day 14, however, changes in the DNA fingerprint between nZVI samples and ZVI samples were clear, indicating nano-specific effects on soil microbes. Finally, one of the intense bands observed on nZVI-100 on day 3 is still present on day 14 indicating enrichment of certain microbes in the sample.

Although in general we did not observe nano-specific toxicity in our studies, the findings of significant effects of iron (bulk and nano) exposure to shoot length and biomass in barley and on microbial diversity may have wider implications on vegetation, crops and soil health in/around the injection sites or in cases of accidental spillage. This study demonstrates that further investigation on the effects of nanoparticles to various environmental receptors are needed before full implementation of such technologies in the field.

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Table 1: Acute and sublethal effects from exposure to nZVI on select aquatic and terrestrial receptors.

Environmental Receptors		Environment Canada Method	Parameters[1]					
			Acute Effects[2] [yes/no][3]		Sublethal Effects[2]			
					Reproduction [yes/no][3]		Biomass [yes/no][3]	
			Nano	Bulk	Nano	Bulk	Nano	Bulk
Terrestrial	**Barley** Shoot Length	EPS 1/RM/45	Yes	Yes	ND[4]	ND	Yes	Yes
	Root Length		No	No	ND	ND	No	No
	Emergence		No	No	ND	ND	ND	ND
	Earthworms	EPS 1/RM/43	No	No	No	No	No	No
Aquatic	**Hyalella**	EPS 1/RM/33	No	No	ND	ND	No	No
(sediments)	**Chironomid**	EPS 1/RM/32	No	No	ND	ND	No	No

[1]Experimental Set up: Nanoscale zero valent iron (as prepared by Golder Associates Ltd. was compared to the bulk sample (BASF ZVI 200). Treatments were run at 100% (2g/L concentration), 50% and 25% for both the nanoscale and bulk samples; Controls included a DRO negative control and two background controls (Food grade dispersant; Palladium: catalyst). Only results for the 100% treatments are shown. [2]Experimental results were compared to the Negative Control. [3]yes – denotes that treatment samples were significantly different from the negative controls; no – denotes that the treatment samples were not significantly different from the negative controls. [4]No Data – Parameter not measured

Figure 2: nZVI for site remediation – Field Scale Study

Location	Quebec Canada (4 km plume, 8 injection points)
COC	TCE
Max[TCE]	690 ug/L
Amount BNP used	4000 kg
Results	↓[TCE]: 50-60% (1 month post injection) >80 (3 months post injection

Above: R. Baig, M. Borda, F. Gheorghui.
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Right: Conceptual site model for nZVI injections (Quebec Canada)

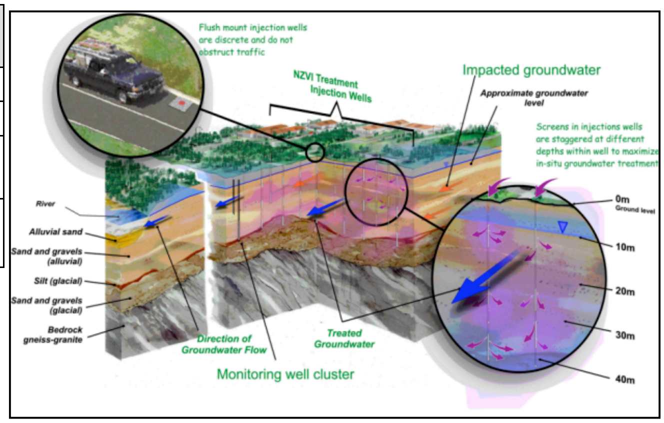
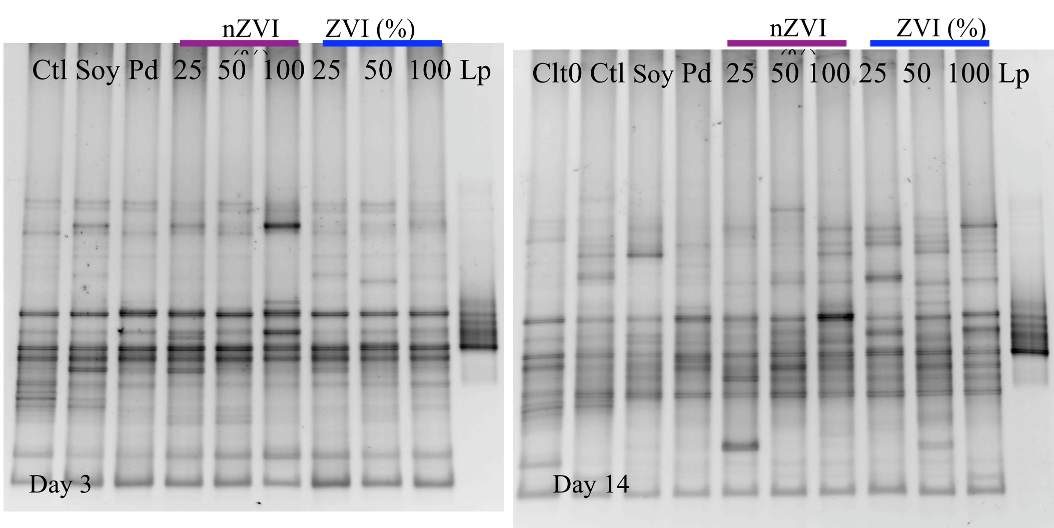


Figure 2. Changes in Soil Microbial Profile after Treatment with nZVI (DNA profiling)\



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