Nano-aluminum: Transport through sand columns and environmental effects on plants and soil communities

Reeti Doshi\textsuperscript{a}, Washington Braida\textsuperscript{a,*}, Christos Christodoulatos\textsuperscript{a}, Mahmoud Wazne\textsuperscript{a}, Gregory O’Connor\textsuperscript{b}

\textsuperscript{a}Center for Environmental System, Stevens Institute of Technology, Hoboken, NJ 07030, USA
\textsuperscript{b}US Army, Environmental Technology Division, Picatinny, NJ 07806, USA

Received 7 December 2006; received in revised form 20 April 2007; accepted 22 April 2007
Available online 29 May 2007

Abstract

Nano-aluminum is being used in increasing quantities as energetic material. This research addresses the transport of two types of nanosized aluminum particles (with aluminum oxide, or carboxylate ligand coating, Alex and L-Alex, respectively) through sand columns along with associated environmental impacts on soil systems. Surface phenomena and pH are variables controlling the transport of nano-aluminum particles through porous media. pH environment controls solubility and electrostatic interactions between nano-aluminum particles and porous media. (i.e., changes in point of zero charge, agglomeration, etc.). Concentrations (up to 17 mg/L) far greater than the World Health Organization guideline for Al in drinking water (0.2 mg/L) were measured in columns’ leachates. Plant uptake studies, mineralization of radiolabeled glucose test and Microtox test were used to investigate the environmental impacts of nano-aluminum on soil communities and plants. It appears that the presence of nano-aluminum particles did not have an adverse effect on the growth of California red kidney bean (\textit{Phaseolus vulgaris}) and rye grass (\textit{Lolium perenne}) plants in the concentration range tested. California red beans did not show uptake of aluminum, while the situation was different for rye grass where a 2.5-fold increase in Al concentration in the leaves was observed as compared with control tests. Nano-aluminum particles in suspension do not appear to have an impact on the metabolic activity of \textit{Vibrio fischeri}. However, when the nano-aluminum particles were amended to the soil, Alex aluminum resulted in a 50% reduction of light output at concentrations below 5000 mg/L soil suspension concentration while L-Alex showed a similar effect at around 17,500 mg/L and the control soil at 37,500 mg/L. Soil respiration studies show that there are not statistical differences between the time and sizes of peaks in CO\textsubscript{2} production and the total mineralization of glucose.

*Corresponding author. Fax: +1 201 216 8303.
E-mail addresses: rdoshi2@stevens.edu (R. Doshi), wbraid@stevens.edu (W. Braida), christod@stevens.edu (C. Christodoulatos), mwazne@stevens.edu (M. Wazne), goconnor@pica.army.mil (G. O’Connor).

\textsuperscript{2}2007 Elsevier Inc. All rights reserved.

Keywords: Nano-aluminum; Transport; Plant uptake; Soil respiration; Microtox

1. Introduction

The development of nanotechnology and the manufacture of new organic and inorganic nanosized materials may result in the release of substantial amounts of these materials into the environment. The fate and transport of nanosized materials, once they are released into the environment, has not yet been fully addressed, nor have the impacts of those materials on plants and soil communities (Leacoonet et al., 2004; Dionysiou, 2004). Nano-aluminum is being used in increasing quantities as energetic material (Argonide, 2004; Novrotsky, 2003; Mench et al., 1998; Fischer and Grubelich, 1998). Aluminum nanoparticles are the basis for superior fuels for space launch vehicles and other rockets or missiles. A single Space Shuttle launch requires approximately 226,800 kg of Al, all in the form of particles with sizes greater than 10\textmu m. Replacement by the faster-burning nano-aluminum particles in the Space Shuttle’s solid rocket boosters will allow motors to be packed more efficiently, which may reduce motor size and thereby increase mission payload. Virtually all food, water, and air contain some aluminum which nature is well adapted to handle. It is
reported that Al is poorly absorbed by the body and efficiently eliminated; however, when absorption occurs, Al is distributed mainly in bone, liver, testicles, kidneys, and brain. Aluminum has been linked to Alzheimer’s disease (dialysis dementia). The respiratory system appears to be the primary target following inhalation exposure to Al (US DHHS, 1999; Sharma and Mishra, 2005). Toxicity of dissolved aluminum to aquatic organisms has been reported (Ward et al., 2005). Aluminum cation (Al$^{3+}$) is very unfriendly to agriculture as it injures plant root cells and thus interferes with root growth and nutrient uptake in crops (Zeng et al., 2006). Most aluminum-containing compounds have low solubility in water unless the water is acidic. This research explores the fate and transport of two types of nano-aluminum particles in subsurface environments as well as potential environmental impacts of these particles. The nano-aluminum particles used for this research were 100 nm in size. Novrotsky (2003) stated that nanoparticles with sizes in the 1–100 nm range (as the ones used in this work) lie in the realm between dissolved molecular clusters and crystalline macroscopic solids and their properties are different from those two.

2. Materials and methods

2.1. Column study

2.1.1. Nano-aluminum particles in suspension

In this study, two types of nano-aluminum particles were used, Alex and L-Alex. Alex nano-aluminum is a metal powder produced by the electroexploded wire technique and then passivated with air to produce a coating of aluminum oxide. L-Alex nano-aluminum is a metal powder produced by the same electroexploded wire technique and then passivated with a carboxylic acid to produce surface carboxylate ligands chains extending outward from the metal surface. The powders are somewhat agglomerated. The agglomerate size is in 1–10 μm range. Six glass columns (Kontes, Vineland, NJ, USA) of 1.5 cm diameter were filled with approximately 20.7 g of Sigma Aldrich silica sand to a height of 16 cm. The porosity of the packing media in the column was characterized (i.e., total heavy metals content, texture, TOC, nitrogen, Hydrogen (ASTM D5373/ D5291) 0.51%

2.2. Plant uptake studies

California red kidney bean plants (Ward’s Biology catalog, 86V8013) and ryegrass (Ward’s Biology catalog, No. 86V8130, Rochester, NY, USA) were grown in the presence of increasing concentrations of Alex and L-Alex nano-aluminum particles. Soil was collected from the campus of Stevens Institute of Technology and passed through a 2 mm sieve to remove pebbles, roots, worms, and vegetation. The soil was fully characterized (i.e., total heavy metals content, texture, TOC, nitrogen, Toxicity Characteristic Leaching Procedure (TCLP) (1992), dissolved phosphorus, pH, and moisture content) to make sure that it was suitable for plant growth. Results are summarized in Tables 1–3.

For each plant species, 200 g soil aliquots were weighed in plastic beakers and then amended with nano-aluminum particles (Alex or L-Alex) to achieve concentration levels of 10, 100, 1000, and 10,000 mg/kg. Control containers were prepared without nano-Al amendment. Then, four ryegrass seeds or two California red kidney bean seeds were planted.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (ASTM 5291)</td>
<td>3.67%</td>
</tr>
<tr>
<td>Hydrogen (ASTM D5373/ D5291)</td>
<td>0.51%</td>
</tr>
<tr>
<td>Nitrogen (ASTM D5373/ D5291)</td>
<td>&lt;0.5%</td>
</tr>
<tr>
<td>Nitrogen—Kjeldahl (EPA 351.3)</td>
<td>0.14%</td>
</tr>
<tr>
<td>Carbon (as carbon) (ASTM D5373/ ASTM D5291)</td>
<td>12%</td>
</tr>
<tr>
<td>Moisture content (gravimetric, 105 °C)</td>
<td>6.1 mg/kg</td>
</tr>
<tr>
<td>pH (ASTM D4972)</td>
<td>6.31</td>
</tr>
<tr>
<td>Texture/color (Munsell chart)</td>
<td></td>
</tr>
<tr>
<td>Moist</td>
<td>10YR 3.5/2</td>
</tr>
<tr>
<td>Dry</td>
<td>10YR 4.5/2</td>
</tr>
</tbody>
</table>

Table 1

Stevens Institute of Technology soil properties
3. Results and discussion

3.1. Column study with nano-aluminum suspensions

When suspensions of nano-aluminum particles were fed into the sand columns, they almost immediately spread through the sand bed. The mobility of both nanoparticles appears to be larger at pH 4 than at pH 7 (Fig. 1). The amount of aluminum leaching out the column for Alex suspension at pH 4 reached a plateau, while the amount for the L-Alex suspension shows a constant increase. This difference may be due to formation of Al(OH)₃ by chemical reaction between Al (Al/Al₂O₃ coated) and water, and due to carboxylic coating. Hydrogen gas formation was observed in the sand bed for Alex, this is believed to be due to Al dissolution. Changes in the color of the Al in the columns and flasks from gray to white were also observed. Peak concentrations of 17 and 10 mg/L of aluminum were measured in the pH 4 column leachate for Alex and L-Alex, respectively (data not shown).

The reaction between elemental aluminum and water may be described by the following reaction:

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}^3+ + 6\text{OH}^- + 3\text{H}_2\text{O} \]  \hspace{1cm} (1)

2.3.2. ¹⁴C-radiolabeled glucose: mineralization studies

Triplet samples of 10 g of soils used in the plant uptake experiments were amended with 5000 mg/kg of Alex or L-Alex. The soil samples were also amended with 20 mL of glucose solution prepared by adding 6.25 g of glucose and 130 µL of ¹⁴C-radiolabeled glucose to 250 mL of DI water. The soil suspensions were placed in 125 mL Erlenmeyer flasks containing a CO₂ trap, made by filling a test tube with 3 mL of 0.5 M NaOH. The content of the trap was removed at given time intervals to measure the amount of radiolabeled CO₂ resulting from glucose mineralization using a scintillation counter. Fresh NaOH solution was placed in the trap through a special Mininert® valve. The total amount of ¹⁴C added to each reactor was equivalent to 1.967 × 10⁻⁷ µCi (43,660 disintegrations per minute).

2.3. Effect of nano-aluminum on soil microbial activity

Two different experimental techniques were used to further assess the potential impacts of nano-aluminum release into the environment. These procedures were (i) Microtox, and (ii) kinetics of mineralization of ¹⁴C-radiolabeled glucose.

2.3.1. Microtox analysis

The Microtox acute test allows assessing the potential toxicity of a liquid or solid sample by measuring the decrease in the light output produced by bacteria, under specific test conditions. Toxicity is reported as IC₅₀, that is, the concentration of contaminant producing a 50% reduction in light output at time t. Suspensions of nano-aluminum materials (Alex or L-Alex), 100 mg/L, were prepared in DI water for testing using the Microtox apparatus. The test protocol used was Microtox 81.9% Basic Test.

To assess the toxicity of nano-aluminum-amended soils the Microtox Basic Solid-Phase Test (BSPT) was performed as follows. Soil suspensions (5 g of soil in 35 mL of DI water) were prepared using the soils amended with 10,000 mg/kg of nano-aluminum (Alex and L-Alex) similar to the one utilized in the plant uptake experiment. The suspensions were shaken and aliquots were tested using the Microtox apparatus.

2.2.1. ¹⁴C-radiolabeled glucose: mineralization studies

Triplet samples of 10 g of soils used in the plant uptake experiments were amended with 5000 mg/kg of Alex or L-Alex. The soil samples were also amended with 20 mL of glucose solution prepared by adding 6.25 g of glucose and 130 µL of ¹⁴C-radiolabeled glucose to 250 mL of DI water. The soil suspensions were placed in 125 mL Erlenmeyer flasks containing a CO₂ trap, made by filling a test tube with 3 mL of 0.5 M NaOH. The content of the trap was removed at given time intervals to measure the amount of radiolabeled CO₂ resulting from glucose mineralization using a scintillation counter. Fresh NaOH solution was placed in the trap through a special Mininert® valve. The total amount of ¹⁴C added to each reactor was equivalent to 1.967 × 10⁻⁷ µCi (43,660 disintegrations per minute).

Fig. 1. Cumulative mass of Al passing through the sand columns fed with Alex and L-Alex nano-aluminum suspensions.
The dissolution of metallic aluminum results in the generation of dissolved aluminum cation concomitant with increases in the concentration of hydroxyls ions and hydrogen gas. Dissolved aluminum may combine with hydroxyls ions to form aluminum hydroxide precipitate.

Both Al suspensions at an initial pH of 4 show an increase in the pH in the effluent (5 < pH < 6) likely resulting from the dissolution of Al, while the control and suspensions originally at pH 7 resulted in very large losses of Al to the hoses and flasks before reaching the column. Furthermore, a major portion of incoming Al particles is retained in the top layer of the sand bed. Mass balance was performed for aluminum by acid washing of flasks, digestions of aliquots of hoses, and measuring Al in effluent and in sand. The mass recoveries were 96.8%, 92.2%, 113%, and 79% for Alex pH 4, Alex pH 7, L-Alex pH 4, and L-Alex pH 7, respectively.

3.2. Column study with nano-aluminum mixed with sand in column

The first set of experiments was run by placing a thin layer of nano-aluminum at the top of the sand bed. From the second day on, the columns amended with Alex nano-aluminum showed signs of gas generation. When the gas comes through the top 1 cm layer of the sand, it causes flotation of this layer that carries the nano-aluminum particles to the top. After 2 days, Alex-amended columns were clogged blocking the passage of leaching solution. The top layer was loosened and the pH 7 solution passed through. However, much less solution passed through the Alex columns receiving solution at pH 4.

The solubility of Al$^{3+}$ is controlled by the formation of amorphous Al(OH)$_3$; once Al(OH)$_3$ is aged it can transform to less soluble aluminum hydroxide phases such as bayerite and gibbsite. Upon further aging the hydroxide phases could transform to various aluminum oxyhydroxide and aluminum oxides. Bayerite was identified in many XRD patterns of the Alex experiments (data not shown). The solubility of Al$^{3+}$ with respect to amorphous Al(OH)$_3$ and bayerite is shown in Fig. 4. Al$^{3+}$ is very soluble at pH values less than 4, the solubility then decreases and it reaches a minimum at approximately pH 6. Al$^{3+}$ solubility then increases as pH is increased. The solubility of Al$^{3+}$ is almost one order of magnitude lower with respect to bayerite than with respect to amorphous Al(OH)$_3$ (Hemingway et al., 1978; Snoeyink and Jenkins, 1980).

Fig. 5 presents the variation of pH in the leachate. As it can be seen, the pH of the leachate from the L-Alex-amended columns did not significantly differ from the pH of the control non-amended columns, suggesting that
L-Alex did not react with the leaching solution. pH of the Alex-amended column increased significantly, likely as a result of Al dissolution. Fig. 6 presents the amount of aluminum leached out from the column. In agreement with the pH results and the clogging pattern, only the columns amended with Alex nano-aluminum show leaching of aluminum. Alex leaches out more at pH 7 than at pH 4, a behavior that differs from the one observed in the previous experiment. The pH in the effluent of the Alex columns stabilizes at a value close to 9 between 0.1 and 0.2 L of eluent. After that, the value decreases to 8 and 6.5 for eluents at initial pH 4 and 7, respectively. The amounts of Al leached out can be explained by the following behavior. For solution pH to change from 4 to 8, the system should go through pH of lowest Al solubility (i.e., pH 6, Fig. 4). Conversely, for a starting pH value of 7, going through Al pH of minimum solubility is avoided.

Since Alex leached more Al in the aforementioned experiment, it is expected that less Al and more L-Alex Al will be retained in the columns. Fig. 7 presents the distribution of aluminum through the column profile after the experiment was terminated. As shown in Fig. 7, both nano-aluminum products traveled along the column profile, although L-Alex did not produce any measurable concentration of Al in the leachate. This may be an indication of a larger retardation factor for L-Alex as compared to Alex due to the organic ligand coating of the particles. This is also evident by the creeping increase in mass of Al eluted for L-Alex column as shown in Fig. 8.

When nano-Al/sand layer was sandwiched between sand beds and eluted with 0.01 M NaCl solution, Alex effluent showed a peak of high pH value corresponding to highest concentration of Al in leachate. L-Alex did not show this kind of behavior. Results of concentration of Al in effluent and cumulative mass leaching at pH 4 and pH 7 are shown in Figs. 8 and 9. The concurrent increase in dissolved aluminum and pH could be attributed to the abundance of both Al$^{3+}$ and OH$^-$/CO$_3^{2-}$ species before the onset of precipitation of Al(OH)$_3$. Once an Al(OH)$_3$ precipitate is formed, the concentration of both of these species decrease as shown in Figs. 5 and 9.

The experimental results show that nano-Al particles coated with Al$_2$O$_3$ (Alex) leached out larger amounts of Al than L-Alex particles. The formation of Al(OH)$_3$ resulted in a decrease in aluminum concentration in the column’s effluent. For the same material, Alex leaches out more at pH 7 than at pH 4, whereas L-Alex leaches out more at pH 4 than at pH 7. L-Alex negative surface charge, due to the carboxylate ligands, may be partially neutralized at pH 4, facilitating its transport through the column. Again, this is a different behavior than the behavior observed when the columns were treated with nano-Al suspensions but similar to the one found in the previous experiment when the columns were amended with thick layers of nano-aluminum. This change in behavior may be related to the ability of nano-aluminum particles to partially dissolve some
metal in the well-stirred suspension and the influence of this dissolved aluminum in the overall transport through the sand column (it seems that for the permeation experiments with Alex suspension, extensive dissolution and precipitation may have occurred in the beaker in addition to the adsorption to all walls).

The point of zero charge (PZC) of Alex was measured with a Malvern Nano Zetasizer. The PZC was found to be around pH 5.9. The PZC of silica sand is between pH values 2 and 2.5. This difference in surface charge may also be partially responsible for the different behavior observed at pH 4 and pH 7 and between transport of Al suspensions and deposited Al (i.e., different interplay among electrostatic charges, solubility, and precipitation).

3.3. Plant uptake studies

During the first experiment, visual observation suggests that plant growth (especially beans) was faster and stronger in the soils amended with both types of nano-aluminum as compared to the plants growing in non-amended soil. However, there was no appreciable difference in growth rate amongst the different nano-aluminum amendment levels. California red kidney beans do not uptake more Al as a result of amending soils with nano-Al particles. Aluminum concentration in the leaves and stems for the soils amended with 10,000 mg/kg of Alex were $517 \pm 17$ and $558 \pm 106$ mg/kg, respectively, and those values do not differ significantly from the values obtained for the control (non-amended) soils ($689 \pm 30$ and $519 \pm 306$ mg/kg for leaves and stems, respectively). Similar results were observed for L-Alex-amended soils. However, the situation is different for rye grass. The concentration of Al in rye grass leaves was on the order of 2750 mg/kg of dry tissue and increased to 3057, 3928, and 4525 mg/kg when the soil was amended with 1000 mg/kg of L-Alex, 10,000 mg/kg of L-Alex, 1000 mg/kg of Alex, and 10,000 mg/kg of Alex, respectively. In the second experiment, no differences in plant growth between aluminum-amended and non-amended control soils were observed. This observation does not necessarily contradict the observations of the previous experiment. A complete evaluation of plant growth requires a very large number of replicates and measurements of dry and humid biomass over time, which was outside the scope of the present work.
The plants grown with addition of DI water and synthetic acidic rainwater at pH 4.2 did not show any significant difference. The results of “dissolved” Al in the lysimeter-collected samples ranged from 0.2 to 1.5 mg/L in containers amended with nano-aluminum and between 0.1 and 1.1 mg/L in non-amended controls. In other words, there were no significant differences between the Al available to plants for the Al-amended and the non-amended soils. In summary, it appears that the presence of nano-aluminum particles did not have an adverse effect of the growth of California red bean and rye grass plants in the concentration range tested. The impact of metals on plant growth is in general plant and soil specific. The buffer capacity of the Stevens’ soil might have played a role in the findings of the current test by offsetting the well-known aluminum plant toxicity in acidic soils. The final soil pH was 6.15.

3.4. Effect of nano-aluminum on soil microbial activity

3.4.1. Microtox analysis

When suspensions of nano-aluminum materials (Alex and L-Alex), 100 mg/L, were tested using the Microtox 81.9% Basic Test, the results obtained for all samples were scattered but the response curves were very flat, suggesting that IC50 should be obtained by extrapolation or in other words that nano-aluminum particles in suspension do not appear to have an impact on the metabolic activity of *Vibrio fischeri*.

For the BSPT, the x-axis in Fig. 10 represents the concentration of soil suspension in the measurement cell and it is clear that the aluminum-amended soils show an effect on light output at a lower concentration than the control soil. This representation of the results takes into consideration the loss of light output due to turbidity of the soil suspension and also takes into consideration any toxicity already present in the soil. According to Fig. 10, Alex aluminum resulted in a 50% reduction of light output at 4500–5000 mg/L soil suspension concentration (roughly equivalent to 50 mg/L of nano-aluminum in the suspension) while L-Alex showed a similar effect at around 17,500 mg/L (nano-aluminum concentration in suspension around 175 mg/L) and the control soil at 37,500 mg/L, suggesting a stronger toxic effect on bacteria for Alex-containing soil when compared to L-Alex-containing soil. However, the difference in the bacterial response between the Al suspension and Al-amended soil suspension allows room for the hypothesis that the increased toxic response observed in the BSPT may be the result of some synergistic effect between the nano-aluminum and the soil.

3.4.2. 14C-radiolabeled glucose: mineralization studies

The total amount of 14C added to each reactor was 1.967 × 10−2 μCi equivalent to 43,660 dpm (disintegrations per minute). The cumulative release of radiolabeled CO2 is presented in Fig. 11 (average of three reactors). Fig. 11 suggests that the presence of nano-aluminum particles does not have an effect on soil respiration. There are no statistical differences between the time and sizes of peaks in CO2 production and the total mineralization of glucose between the nano-aluminum samples and the control sample.
Acknowledgments

This study was supported by TACOM/ARDEC, Pica-tinny Arsenal under Contract DAAE30-00-D-1011, Task #23.

References


US Department of Health and Human Services, 1999. Toxicological Profile for Aluminum. ASTDR.
