

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

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## 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 (*Phaseolus vulgaris*) and rye grass (*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 *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<sub>2</sub> production and the total mineralization of glucose.

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## 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 (Leacoanet 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 μm. 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

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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 ( $\text{Al}^{3+}$ ) 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  $\mu\text{m}$  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 estimated from the bulk density to be approximately 0.52, with an average column void volume of about 8.7  $\text{cm}^3$ . The pH of two 1 L aliquots of 0.01 M NaCl solutions was adjusted to 7.0 and 4.0 using 0.1 M solutions of  $\text{NaHCO}_3$  and HCl, respectively. The pH values selected bracket the prevailing pH range in the field. Each aliquot was split into three bottles, one of which was kept intact to be run through the control column and the others were amended with Alex and L-Alex nano-aluminum to obtain suspensions with initial concentrations of 50 mg/L. Nanoparticle dispersion was achieved using an ultrasonic water bath and during the run, Al particles were kept in suspension using magnetic stirrers. The solutions and the Al suspensions were pumped intermittently through the columns at a flow rate of 15 mL/h for 4 h each day. All the effluent from the columns was collected. The effluent aluminum concentration was measured after microwave-assisted acid digestion of aliquots of leachate. This was necessary to maintain the consistency of the research protocol through the whole project because the nature (i.e., size) of nanoparticles and dissolved species are differentiated by filtration through 0.2 or 0.45  $\mu\text{m}$  filters. In the case of nanoparticles, the particle size is on the order of 100 nm (or 0.1  $\mu\text{m}$ ) and this makes the previous operational definition irrelevant. Experiments were interrupted when the water flow through the columns stopped due to clogging of the porous media. At that time, the columns were cut in three sections. The content of each section were thoroughly homogenized and aliquots digested using microwave-assisted

acid digestion. Aluminum in the digestate was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista, Varian Inc., Palo Alto, CA, USA).

#### 2.1.2. Nano-aluminum-amended columns

A second leaching experiment was performed to address the leaching of nano-aluminum particles when they are deposited in soil. Columns similar to the ones described in the previous section were filled with Sigma Aldrich silica sand to a height of 15 cm. Then, a layer of 200 mg of nano-aluminum (Alex or L-Alex) was placed at the top of the column and covered with a 1 cm layer of sand. Solutions of 0.01 M NaCl, at pH 4 or pH 7, were passed through the control columns (columns with sand only) and columns amended with Alex and L-Alex as described in Section 2.1.1. Column effluent was collected daily and digested as described in the previous section before measuring the concentration of Al by ICP-OES. At the end of the experiment, the glass columns were cut into sections and aliquots of the sand contained in the sections below the layer of nano-aluminum were also digested using microwave assisted acid digestion before measuring the concentration of Al by ICP-OES in the digestate. The top layer of Alex and L-Alex were preserved for SEM and X-ray diffraction (XRD) analysis.

The experiment was stopped after passing 300 mL solution as the interactions between the nano-Al layer and the solution caused clogging of the packing media. A new experiment was performed to overcome this limitation by placing a thick layer of aluminum between sand beds. Similar glass columns were filled with a 5 cm thick Al/sand mixture sandwiched between two 5 cm layers of sand. This mixture resulted in 80 mg of aluminum contained on a 5 cm layer of Al/sand mixture. A 0.01 M NaCl solution adjusted to pH 4 or 7 was passed through these columns. Effluent from the columns was collected and digested using microwave acid digestion. Aluminum concentration in the leachate was measured by ICP-OES. pH of the effluent was measured after collection.

### 2.2. Plant uptake studies

California red kidney bean plants (Ward's Biology catalog, 86V8013) and rye grass (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 rye grass seeds or two California red kidney bean seeds were planted

Table 1  
Stevens Institute of Technology soil properties

Property	Value
TOC (ASTM 5291)	3.67%
Hydrogen (ASTM D5373/ D5291)	0.51%
Nitrogen (ASTM D5373/ D5291)	<0.5%
Nitrogen—Kjeldahl (EPA 351.3)	0.14%
Carbon (as carbon) (ASTM D5373/ ASTM D5291)	
Moisture content (gravimetric, 105 °C)	12%
Soluble phosphate (EPA 365.2)	6.1 mg/kg
pH (ASTM D4972)	6.31
Texture/color (Munsell chart)	
Moist	10YR 3.5/2
Dry	10YR 4.5/2

Table 2  
Sieve analysis

Screen/opening	% Retain	Cumulative % retain
#20/0.85 mm	28.1	28.1
#40/0.425 mm	25.8	53.9
#60/0.25 mm	18.2	72.1
#200/0.075 mm	22.8	94.9
#400/0.038 mm	4.3	99.2
Pan	0.8	100
$D_{10}$	0.1 mm	
$D_{60}$	0.57 mm	
Coefficient of uniformity	5.7	

Table 3  
Total heavy metal content in mg/kg of soil (microwave extraction, ICP-OES, EPA 6100 and EPA 200.7)

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Pb	S	Si
Average	12621	64.9	2121	6.43	15578	1216	2432	198	137	66.3	285	1680
Std. dev.	2575	8.3	261	2.38	1519	432	305	16	49	28.4	37	1325

Average and standard deviation of six replicates.

in each container. Plants were watered daily, and the effects of nano-aluminum on the plant growth were observed and recorded. All experiments were run in duplicates. The experiment was run for 2 months. At the end of the experiment, the aluminum concentration in the bulk soil, rhizosphere soil (including roots), shoots, and leaves was measured with ICP-OES after microwave-assisted acid digestion to assess the fate of nano-aluminum in these systems. Due to the low dry mass yield of the rye grass, rhizosphere and leaf fractions of the two replicates were combined to form a composite sample before acid digestion.

A second experiment was run in which concentration of Al amendment in soil was fixed at two levels, 500 and 5000 mg/kg. Triplicate samples were run for each concentration level. Replicates were watered with deionized (DI) water or synthetic acidic rainwater. The latter was prepared by adding drop by drop 3:2  $H_2SO_4:HNO_3$  0.1 M solution to DI water until it reached a final pH of 4.2. Stevens's soil has moderate pH-buffering capacity. Mini lysimeters were used to collect water samples from the soil to measure amount of 'dissolved' aluminum.

### 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  $^{14}C$ -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  $IC_{50,t}$ , 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.

#### 2.3.2. $^{14}C$ -radiolabeled glucose: mineralization studies

Triplicates of 10 g aliquots of the soil 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  $\mu$ L of  $^{14}C$ -radiolabeled glucose to 250 mL of DI water. The soil suspensions were placed in 125 mL Erlenmeyer flasks containing a  $CO_2$  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  $CO_2$  resulting from glucose mineralization using a scintillation counter. Fresh NaOH solution was placed in the trap through a special Mininert<sup>®</sup> valve. The total amount of  $^{14}C$  added to each reactor was equivalent to  $1.967 \times 10^{-2} \mu$ Ci (43,660 disintegrations per minute).

## 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 Alex ( $Al/Al_2O_3$  coated) and water, which may occur at a smaller scale or does not take place with L-Alex, 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:

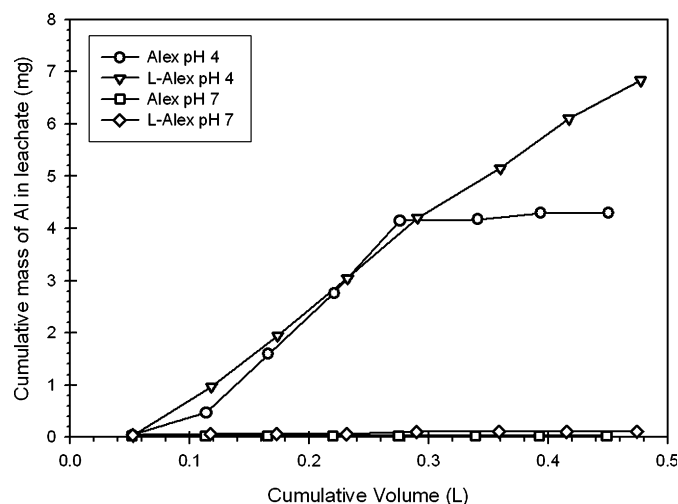
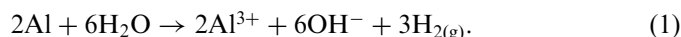


Fig. 1. Cumulative mass of Al passing through the sand columns fed with Alex and L-Alex nano-aluminum suspensions.

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 ( $5 < \text{pH} < 6$ ) likely resulting from the dissolution of Al, while the control and suspensions originally at pH 7 resulted in leachates with a fairly constant and slightly lower pH (Fig. 2). The leaching behavior presented in Fig. 1 and the information on amounts of Al retained in the columns presented in Fig. 3 suggest that suspensions 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

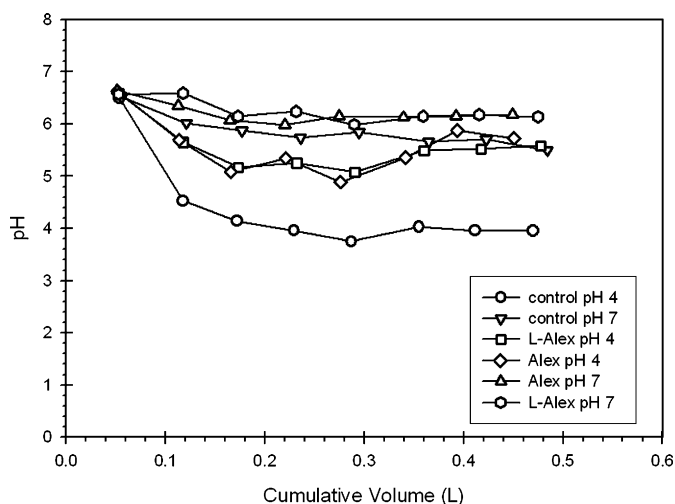


Fig. 2. pH of the effluent from sand columns feed with Alex and L-Alex nano-aluminum suspensions.

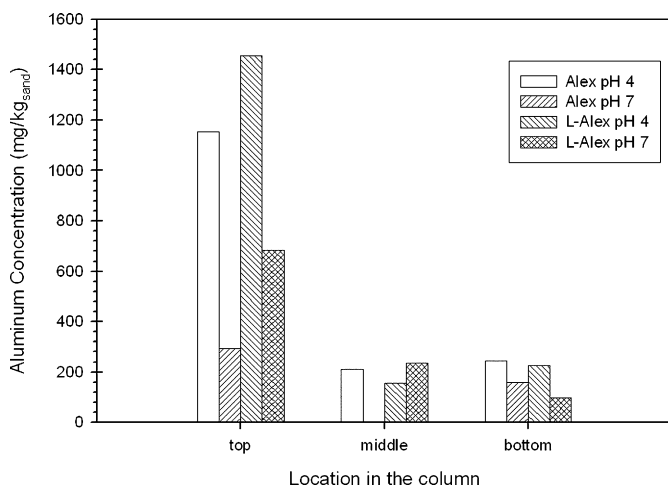


Fig. 3. Aluminum concentration along the column profile after the termination of the experiment of Al suspension permeation through the sand columns. Top portion varies from 4.8 to 6.2 cm from the top, middle portion ranges between 4.8 and 5.4 cm from the end of the top portion, and bottom portion includes the last 5.5–6.2 cm of sand in the column.

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  $\text{Al}^{3+}$  is controlled by the formation of amorphous  $\text{Al}(\text{OH})_3$ ; once  $\text{Al}(\text{OH})_3$  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  $\text{Al}^{3+}$  with respect to amorphous  $\text{Al}(\text{OH})_3$  and bayerite is shown in Fig. 4.  $\text{Al}^{3+}$  is very soluble at pH values less than 4, the solubility then decreases and it reaches a minimum at approximately pH 6.  $\text{Al}^{3+}$  solubility then increases as pH is increased. The solubility of  $\text{Al}^{3+}$  is almost one order of magnitude lower with respect to bayerite than with respect to amorphous  $\text{Al}(\text{OH})_3$  (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

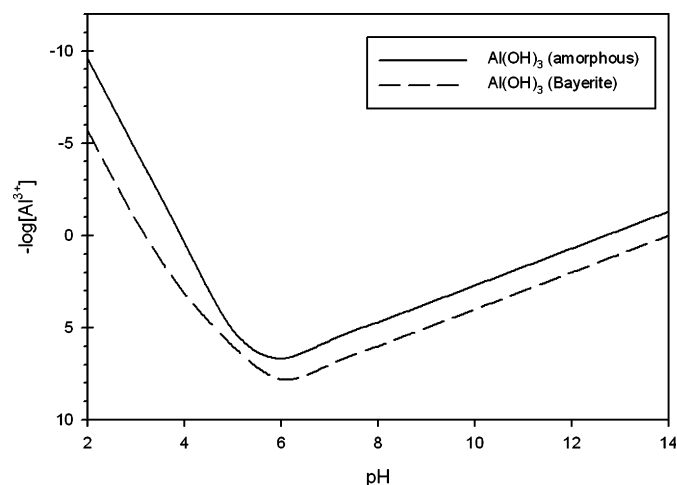


Fig. 4. Solubility diagram for  $\text{Al}(\text{OH})_3$ , bayerite, and amorphous.

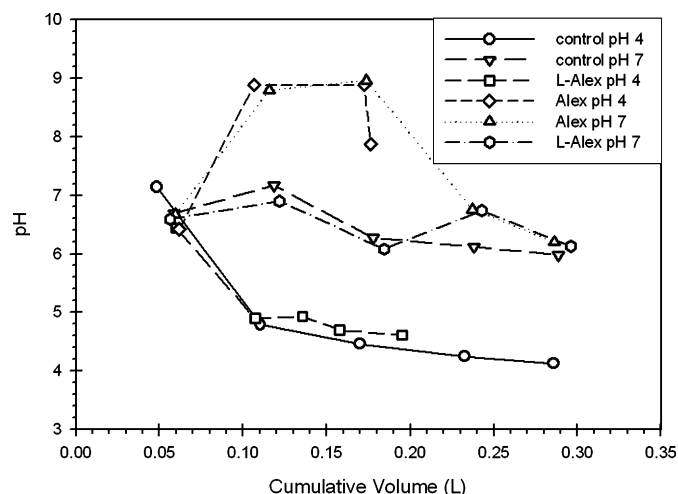


Fig. 5. pH of the effluent from sand columns amended with Alex and L-Alex nano-aluminum.

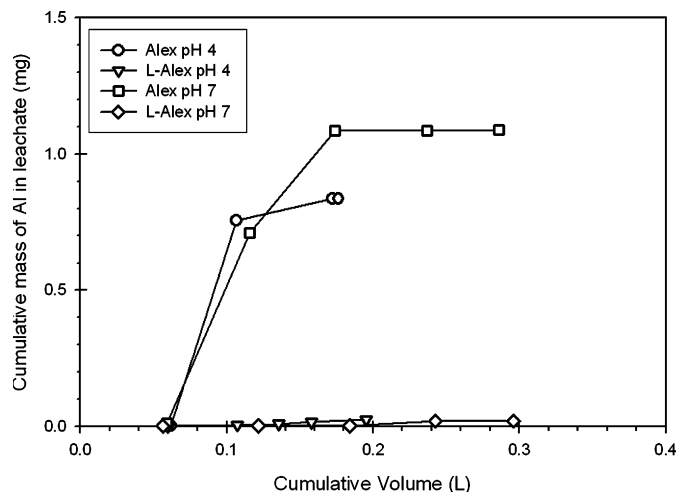


Fig. 6. Cumulative mass of Al passing through the sand columns amended with Alex and L-Alex nano-aluminum.

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

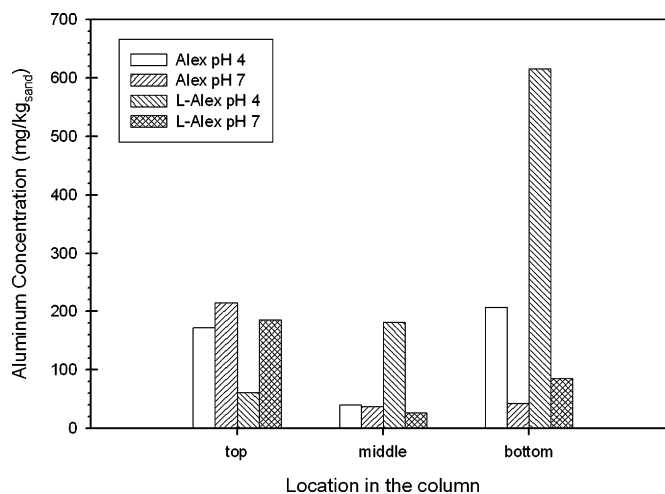


Fig. 7. Aluminum concentration along the column profile after termination of the experiment with Al layers sandwiched between sand layers in the columns. Each section is 5 cm in length.

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  $\text{Al}^{3+}$  and  $\text{OH}^-$  species before the onset of precipitation of  $\text{Al}(\text{OH})_3$ . Once an  $\text{Al}(\text{OH})_3$  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  $\text{Al}_2\text{O}_3$  (Alex) leached out larger amounts of Al than L-Alex particles. The formation of  $\text{Al}(\text{OH})_3$  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

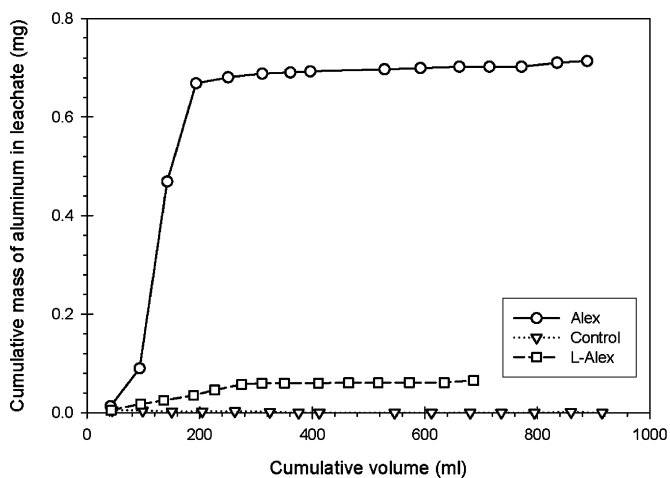
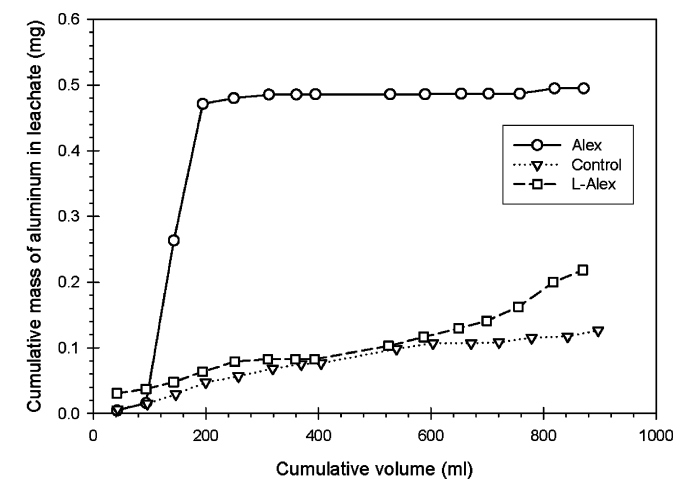


Fig. 8. Cumulative amount of Al in effluent from Al/sand columns eluted with 0.01 M NaCl solution at pH 4 (top) and pH 7 (bottom).

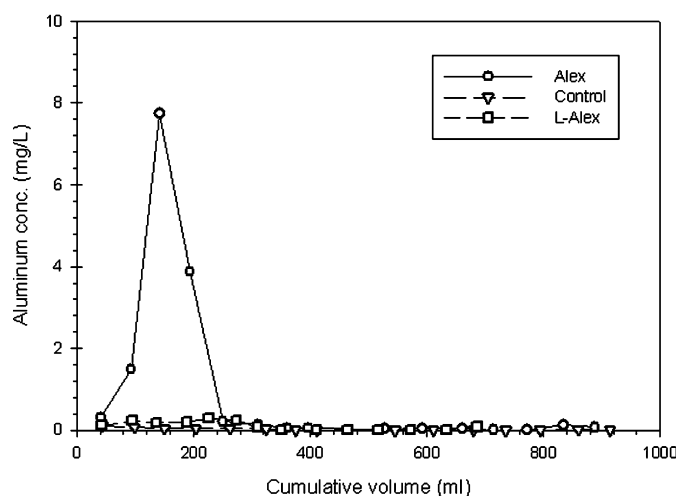
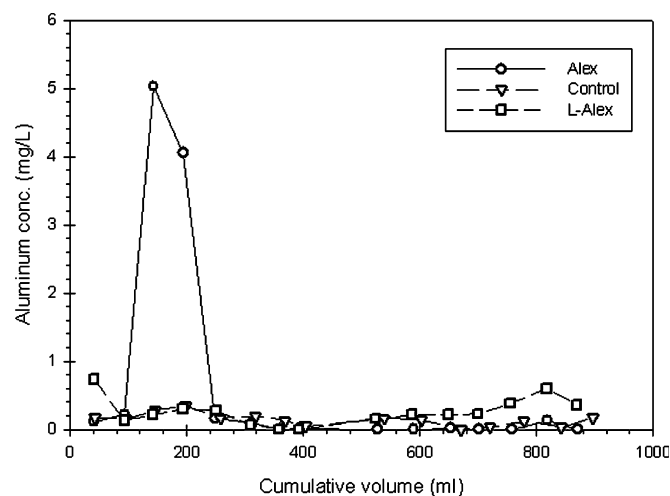


Fig. 9. Concentration of Al in effluent from Al/sand columns eluted with 0.01 M NaCl solution at pH 4 (top) and pH 7 (bottom).

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, 5284, 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  $IC_{50,t}$  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

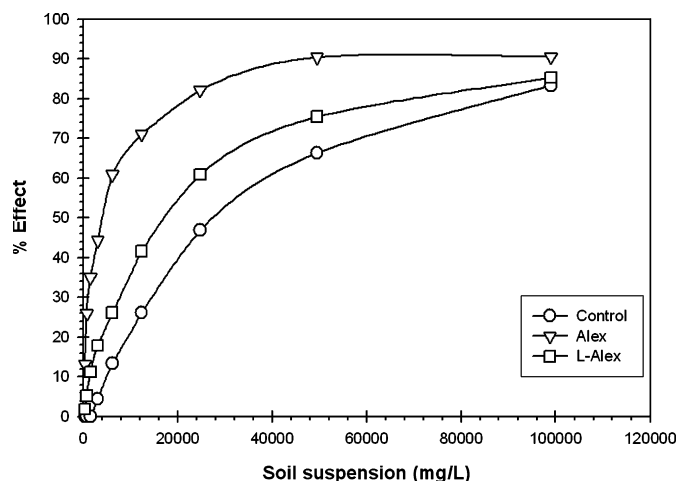


Fig. 10. Microtox Basic SPT response curve.

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. $^{14}C$ -radiolabeled glucose: mineralization studies

The total amount of  $^{14}C$  added to each reactor was  $1.967 \times 10^{-2} \mu Ci$  equivalent to 43,660 dpm (disintegrations per minute). The cumulative release of radiolabeled  $CO_2$  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  $CO_2$  production and the total mineralization of glucose between the nano-aluminum samples and the control sample.

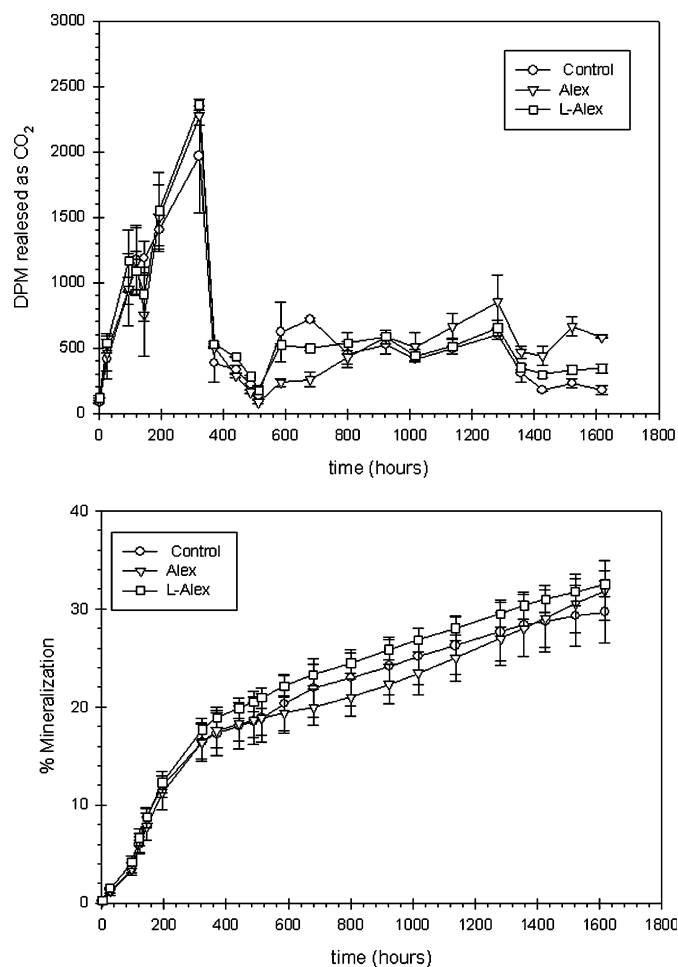


Fig. 11. Time-dependent (top) and cumulative (bottom) release of radiolabeled  $CO_2$ .

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