

Behavior of Engineered Nanoparticles in Landfill Leachate

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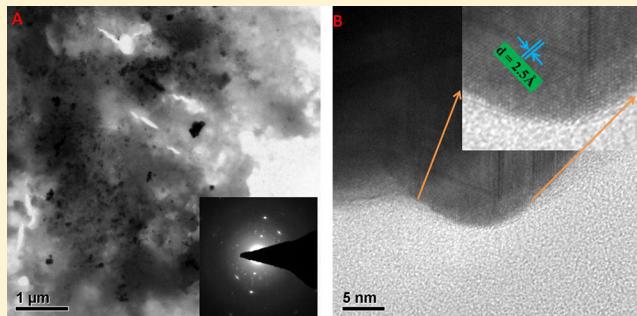
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S Supporting Information

ABSTRACT: This research sought to understand the behavior of engineered nanoparticles in landfill leachate by examining the interactions between nanoparticles and leachate components. The primary foci of this paper are the effects of ZnO, TiO₂, and Ag nanoparticles on biological landfill processes and the form of Zn, Ti, and Ag in leachate following the addition of nanoparticles. Insight into the behavior of nanoparticles in landfill leachate was gained from the observed increase in the aqueous concentrations over background for Zn, Ti, and Ag in some tested leachates attributed to leachate components interacting with the nanoparticle coatings resulting in dispersion, dissolution/dissociation, and/or agglomeration. Coated nanoparticles did not affect biological processes when added to leachate; five-day biochemical oxygen demand and biochemical methane potential results were not statistically different when exposed to nanoparticles, presumably due to the low concentration of dissolved free ionic forms of the associated metals resulting from the interaction with leachate components. Chemical speciation modeling predicted that dissolved Zn in leachate was primarily associated with dissolved organic matter, Ti with hydroxide, and Ag with hydrogen sulfide and ammonia; less than 1% of dissolved Zn and Ag was in the free ionic form, and free ionic Ti and Ag concentrations were negligible.



INTRODUCTION

Over the past decade, engineered particles with nanoscale dimensions have been key to advancements in drug delivery and pharmaceuticals, cosmetics, environmental remediation, nanotechnology, biomaterials, and energy production.^{1–7} Engineered Nanoparticles (NPs) are increasingly used because of their large surface area^{8–10} and unique electronic, optoelectronic, thermal, and catalytic properties.¹¹ Most NPs that are incorporated into consumer products are coated, surface modified, and/or functionalized to achieve specific properties.^{12,13} According to an inventory completed by the Project on Emerging Nanotechnologies, 1317 consumer products containing NPs were available in 2010.¹⁴ Of these products, just over 55% were health and fitness related, but also included electronic components, cosmetics, antibacterial agents, polishing and binding agents, solar cells, and UV-absorbers in sunscreen lotion, among many others.¹⁴

It is estimated that the manufacturing of nanomaterials (NMs) will increase from 1000 to 58 000 tonnes yearly from 2011 to 2020.¹⁵ As NPs are incorporated into consumer products at greater rates, the introduction of these NMs into the solid waste stream is inevitable. Since nanotechnology is still in its early stages, there are currently no regulations

regarding the disposal of NMs; further, little is known about their fate in municipal solid waste (MSW) landfills, the predominant global MSW disposal option.¹² The disposal of nanowastes into landfills raises concern about the effects of the added NPs on anaerobic (waste degradation and leachate treatment) and aerobic (leachate treatment) processes associated with landfills in addition to the potential release of these NPs to the environment through the interaction with landfill leachate.

Therefore, this research sought to understand the behavior of metallic NPs in landfill leachate by examining the interactions between NPs and leachate components; assuming that the NPs had leached from consumer products and were present in the liquid phase. The waste environment is a dynamic and heterogeneous matrix and the leachate produced contains a plethora of constituents that can affect NP behavior. Therefore, leachate is a mobile aqueous phase that, if released, can impact surrounding environments. An additional path for the added

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NPs is the association with the solid waste mass by adsorption which would retain the NPs, which was not the focus of this paper.

Landfill leachate varies significantly from landfill to landfill and from time to time as a function of the composition and depth of solid waste, age of waste, precipitation rates, and landfill design and operations.^{16–21} Organic matter in leachate from young landfills is readily biodegradable as suggested by a high biochemical oxygen demand/chemical oxygen demand (BOD/COD) ratio (>0.70), while organic matter in mature leachate (~from landfills greater than ten years) is characterized by low biodegradability and BOD/COD ratios (typically <0.1).^{20,22–24} Organic matter measured by COD (e.g., humic acid (HA)) can be substantial for many decades (>1000 mg/L). It was anticipated that HA will be the dominant component affecting the stability of NPs²⁵ and there will be minimal differences between the fate of the added NPs in middle-aged and mature leachate, as there is a significant concentration of HA found in leachate regardless of the age.

The primary foci of this study were to evaluate the effect of zinc oxide (ZnO), titanium dioxide (TiO₂), and silver (Ag) NPs on biological landfill processes and the chemical speciation of Zn, Ti, and Ag in landfill leachate. ZnO, TiO₂, and Ag NPs were chosen, as they are commonly found in commercial products. ZnO has been frequently used in sunscreens, because at the nanoscale, ZnO can be transparent in the visible spectrum (390–750 nm) while retaining the ability to block UV rays (290–380 nm).^{11,26} TiO₂ has been traditionally added to paints and cosmetics.^{27,28} It is also used to remediate polluted air and water because of its photocatalytic oxidative properties.^{27,29} Ag NPs are commonly used in electronics, photography, and as catalysts and antimicrobial agents.^{30–32}

MATERIALS AND METHODS

Collection and Chemical Characterization of Leachate Samples

To account for variability in leachate characteristics, multiple leachates were studied representing the inevitable changes in the waste environment over time and the effect these variations might have on the fate of NPs. Leachate was obtained from two conventional MSW landfills (i.e., no leachate recirculation) in Central Florida. Leachate samples were collected directly from a leachate collection lift station at a recently closed landfill cell, which was a source of middle-aged (BOD/COD = 0.1–0.7) leachate. Mature leachate was collected from a transmission pipe at a second landfill that had been operated since the 1960s. All samples were collected in clean high-density polyethylene (HDPE) containers, completely filled to eliminate headspace, and placed on ice during transportation. Leachate was stored at 4 °C until use.

Leachate was characterized for pH, alkalinity, five-day biochemical oxygen demand (BOD₅), COD, conductivity, ammonia-nitrogen, and solids (total and suspended) following Standard Methods for the Examination of Water and Wastewater.³³ Additionally, the dissolved HA concentration was determined after filtering leachate through a 450-nm filter by measuring absorbance, at 254 nm, using an UV-vis spectrophotometer.^{34,35} A humic acid calibration curve was developed using Aldrich HA.

Materials Used. ZnO (Z-Cote HP1) coated with triethoxycaprylylsilane (1–4% w/w) and TiO₂ (T-Lite SF-S) coated with hydrated silica, dimethicone/methicone copolymer, and aluminum hydroxide (20–40% w/w) were procured from BASF (Florham Park, New Jersey). According to the material

safety data sheets (MSDS) and confirmed by high-resolution transmission electron microscopy (HRTEM) analysis ZnO and TiO₂ NPs distribution was 50 to 200 nm in particle size. Ag NPs (#0120XH), coated with polyvinylpyrrolidone (<1% w/w), were purchased from SkySpring Nanomaterials, Inc. The particle distribution of Ag NPs was approximately 10 to 20 nm. Purchased ZnO, TiO₂, and Ag NPs were water insoluble according to their MSDS.

Leachate Exposure to Coated Nanoparticles. NPs were added individually to 4-L glass reactors containing 4 L of different types of leachate (used as collected) for a final NP concentration of 100 µg/L, 1.0 mg/L, and 100 mg/L (total of six reactors); reactors were purged with N₂ to create an anaerobic environment and sealed. Reactors were continuously stirred at room temperature (~24 °C), for up to 60 days to simulate NP weathering that could occur during the long retention time expected in landfills and during leachate treatment. Aliquots of leachate were removed periodically to examine the time effects. Concentration-dependent effects of the added NPs on anaerobic (biochemical methane potential; BMP) and aerobic (BOD₅) biological processes were determined over time. Detailed studies of metal concentrations were also conducted for reactors containing 100 mg/L of added NPs after 30 days of stirring in the absence of oxygen. Results were compared to control reactors treated in the identical manner without the addition of coated NPs.

Size Fractionation of Leachate Samples Exposed to Coated Nanoparticles. Size fractionation of leachate was completed to provide insight into the forms the NPs might take after addition to leachate (suspended, dissolved, or aggregated). Aliquots of approximately 200 mL were periodically taken under continuous stirring from the center of each reactor using a wide-mouth pipet and fractionated, following which the samples were acidified with 2% nitric acid and stored at 4 °C until analyzed. After each sampling event the reactors were purged with N₂ to avoid the addition of oxygen and then resealed. The aliquots were filtered in series using a 1500-nm glass filter (Whatman 934-AH), under vacuum, to capture the suspended and aggregated fraction and a 1.0-nm filter (1000 Nominal Molecular Weight Limit regenerated cellulose), using an Amicon ultrafiltration stir cell (30 psi), to capture what is defined in this study as the dissolved fraction.³⁶ Traditionally, dissolved metals are characterized using a 450-nm filter, but due to the size of the added NPs a smaller size cutoff was used. This method was also conducted for the control reactors.

Metals Analysis of Leachate Exposed to 100 mg/L of Coated Nanoparticles. The concentration of each metal in the leachate fractions (total, <1500 nm, and <1 nm) was quantified using Inductively Coupled Plasma-Optical Emission Spectrum (ICP-OES). The background concentration of Zn, Ti, and Ag in each fraction was also determined before the addition of the coated NPs. The fractionated and acidified samples were digested using concentrated nitric acid and 1:1 water/hydrochloric acid solution, following Standard Method 3030F,³³ to reduce the interference of organic matter during metals analysis. After digestion, samples were filtered using a 450-nm mixed cellulose ester membrane filter and diluted with distilled water to a final volume of 50 mL in a volumetric flask. To evaluate the overall analytical performance of ICP-OES, usability of data, and the effect of the leachate matrix during analysis, both a matrix duplicate and matrix spike (1.0 mg/L of Zn, Ti, and Ag standard) were included.

Table 1. Recovery of NPs Added to Leachate after Seven Days

NP	mass added (volume)	aqueous, mg (% of total mass added)	nonaqueous, mg (% of total mass added)	total recovery, mg	percent recovered
ZnO	41 mg as Zn (500 mL)	1.2 ± 0.53 (2.8% ± 1.3%)	38 ± 0.35 (93% ± 0.85%)	39 ± 0.13	95% ± 0.3%
TiO ₂	8.4 mg as Ti (200 mL)	0.73 ± 0.075 (8.7% ± 0.2%)	5.3 ± 0.69 (63% ± 8.2%)	6.0 ± 0.41	71% ± 1.0%
Ag	19 mg as Ag (200 mL)	1.5 ± 0.078 (7.9% ± 0.2%)	14 ± 3.0 (71% ± 16%)	15 ± 2.8	79% ± 15%

A mass balance study was conducted to evaluate the sampling technique, digestion method, and analytical recovery of NPs added to leachate. A known amount (see Table 1) of NPs was added to reactors (in triplicate) containing mature leachate. After continuously stirring for seven days, an aliquot from each reactor was collected using a wide-mouth pipet, acidified and digested, and then analyzed for each metal. This fraction represented the concentration of aqueous phase metals. To determine the total mass of each metal in the aqueous phase the product of the total volume and aqueous phase concentration was used. Subsequently the remaining volume was acidified and digested and metal concentration measured. This fraction contained the NPs that floated, settled, or adsorbed on the glassware. The sum of the mass of metals in these two fractions, after correcting for background metals, represented the total mass recovered. The mass of "non-aqueous" phase metals was calculated by difference between total mass recovered and aqueous phase metal mass. Table 1 summarizes both the mass in each fraction and the percent recovered for each NP.

Mass balance determination shows reasonable recovery of metals from leachate. Therefore, it was concluded that pipetting allowed us to measure the aqueous fraction of metals (dissolved, suspended, and dispersed) which was the primary focus of the study. However, there was a significant mass of NPs that was not captured by pipetting, presumably located at solid/liquid/gas interfaces (i.e., coating the reactors, floating, or settled) which was an additional fate of the added NPs in landfill leachate.

Chemical Speciation of Dissolved Zn, Ti, and Ag using Visual MINTEQ. The chemical speciation of dissolved Zn, Ti, and Ag in leachate is an important component in understanding the toxicity, mobility, and bioavailability of the metal in the environment. Coupling data generated from size fractionation and leachate characterization, the chemical speciation of metals was modeled using Visual MINTEQ, an equilibrium model that was developed based on USEPA MINTEQ2.³⁷ The model yielded chemical speciation data that were used to determine the form of the dissolved metals, measured after NP addition, in leachate and the percentage of the dissolved metals present in their free ionic state (e.g., Zn²⁺, Ti⁴⁺, and Ag⁺). This information also provided insight into results from bioassays described below. NP toxicity in aquatic systems has been extensively studied but a key challenge of these studies was the lack of information regarding the metal species that were responsible for any toxicity.^{38–40}

The measured total Zn, Ti, and Ag concentration in the fraction less than 1.0 nm was used as an input to model the chemical speciation of Zn, Ti, and Ag. The Gaussian dissolved organic matter (DOM) model, which is integrated into Visual MINTEQ, was used to estimate the distribution of metal complexation sites on DOM⁴¹ based upon the input HA concentration, binding affinity, competition with other metal ions, and input pH.

Visual MINTEQ input parameters used in this study were based on the initial characteristics of the collected leachate

which included pH and concentration of HA, dissolved metals, ammonia-nitrogen, and alkalinity. Sulfate, sulfide, phosphate, chloride, and nitrate concentrations were included in the model inputs due to their importance in dissolved metal complexation; however, average values reported in the literature¹⁷ for mature and middle-aged leachate were used, as they were not measured during the study. Sulfides, which often control the solubility of metals such as Ag under anaerobic conditions, were not measured therefore historical data from one of the landfills were used in the chemical speciation modeling.¹⁷ A sensitivity analysis was completed to understand the effect of sulfide and chloride concentrations on the chemical speciation of Zn, Ti, and Ag (Figures S5–S14) because of the potential importance on metal behavior, particularly Ag.

Effect of Coated Nanoparticles on Biological Processes. The effect of NPs on landfill processes under both anaerobic and aerobic conditions was studied using broad bioassays, BOD_S, and Biochemical Methane Potential (BMP), which are commonly used to examine the biodegradability of wastewaters.^{16,42} Aliquots of 40 mL were removed periodically from reactors using a wide-mouth pipet during continuous stirring and tested for BOD_S and BMP. Any statistically significant ($\alpha = 0.05$) decrease in BOD_S and BMP concentrations relative to control samples would suggest inhibitory effects.

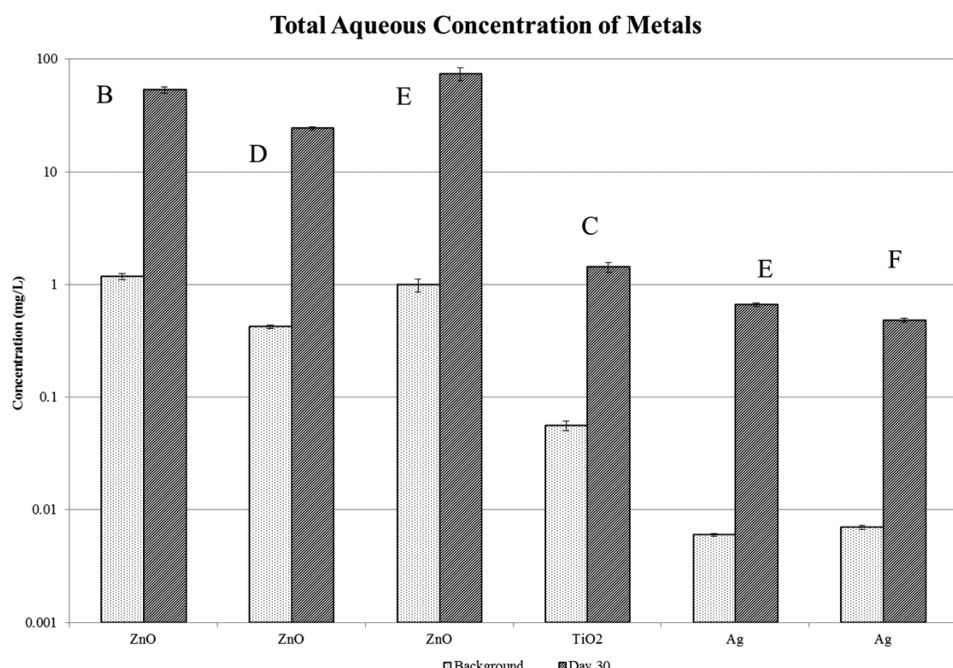
BOD_S was performed following standard methods 5120B.³³ Dilution of leachate was required and ranged from 0.01 to 2 mL:300 mL (leachate:dilution water). All BOD_S tests were seeded with 4 mL of PolySeed. The toxicity of NPs in a glucose-glutamic acid (GGA) solution, without leachate, was also tested by measuring the BOD_S of a 300 mL GGA solution containing 100 mg/L of each NP (separately) after continuously stirring the mixture for seven days. A GGA standard solution without NPs was treated in an identical manner.

The BMP was determined following ASTM method E2170. An anaerobic inoculum medium was prepared by combining anaerobically digested sludge obtained from a local domestic wastewater treatment facility with the necessary nutrients that are required to sustain an anaerobic environment for at least 90 days. BMP assays were prepared individually in 125-mL serum bottles processed under anaerobic conditions (maintained through continuous N₂ flushing). Serum bottles were filled with 5 to 30 mL of leachate after which the anaerobic inoculum was added using a peristaltic pump for a final volume of 100 mL. All bottles were sealed with a rubber stopper and aluminum crimp, and incubated upside down at 35 ± 2 °C.

Gas quantity was determined using a frictionless syringe periodically inserted into the stopper over a 30- to 90-day period until gas production ceased (<1 mL/day). BMP represents the cumulative methane produced over the test period. Additionally, the carbon dioxide (CO₂) and methane (CH₄) concentrations in the headspace were measured using a Shimadzu-14 gas chromatograph equipped with a thermal conductivity detector (TCD) and Carboxen-1000 Column. During analysis the carrier gas was helium (30 mL/min) and

Table 2. Characteristics of Leachate Used in NP Exposure Studies^a

parameters	units	leachate B	leachate C	leachate D	leachate E	leachate F
pH	S.U.	7.5	7.4	7.7	7.5	7.9
COD	mg/L	5790	18 600	17 400	22 600	28 900
BOD	mg/L	618	1320	5850	9080	2400
BOD:COD	-	0.11	0.07	0.34	0.40	0.08
Ammonia-N	mg/L	546	1270	1633	1360	1730
Conductivity	$\mu\text{S}/\text{cm}$	6570	19 727	19 900	N/A	N/A
Humic Acid Concentration	mg/L	310	6470	6500	6500	6000
Alkalinity	mg/L CaCO_3	2200	800	6670	6900	N/A
Total Solids	mg/L	5350	11 700	14 900	13 950	12 540
Total Suspended Solids	mg/L	60	120	100	250	140
Total Dissolved Solids	mg/L	5290	11 580	14 800	13 700	12 400

^aN/A: not available.Figure 1. Comparison of metal concentrations in aqueous phase before and after the addition of NPs (Total) (middle-aged leachate: D,E; mature leachate: B,C,F; TiO₂ data in leachate D is not available).

the detector temperature was held at 250 °C, while the injection temperature was kept at 35 °C for five minutes then ramped, in 20 °C increments, up to 225 °C over a 16-min run time.

RESULTS AND DISCUSSION

Leachate Characterization. The effect of the three NPs on landfill processes was studied using six different landfill leachates representing different stages of waste degradation. From the leachate characteristics, summarized in Table 2, Leachates D and E were classified as middle-aged (BOD:COD = 0.34–0.40), while B, C, and F were found to be mature (BOD:COD = 0.07–0.11). Zn was studied in Leachates B, D, and E; Ti in Leachates C and D; and Ag in Leachates E and F.

Fate of Coated Nanoparticles in Landfill Leachate. Metals found in leachate fractions, differentiated by size cutoffs, were assumed to take one of two forms: (1) nonaqueous NPs (coating the reactor, settled, suspended, or floating at the surface) or (2) aqueous (suspended, dispersed, or dissolved) metals that may be either in a free ionic form or associated with NPs.

The concentration of Zn, Ti, and Ag by size fractionation after the addition of 100 mg/L of ZnO, TiO₂, and Ag NPs was quantified following a 30-day period in mature and middle-aged leachates (Leachates B–F). The total Zn, Ti, and Ag concentrations added were 81, 44, and 99 mg/L, respectively. Background unfiltered aqueous phase concentrations of Zn, Ti, and Ag in leachate and 30 days after NP addition are shown in Figure 1. The aqueous concentrations were less than the added concentration because of the low solubility of these NPs in water; however, dispersion of the coated ZnO, TiO₂, Ag NPs in leachate was observed in all leachates tested. These NPs dispersed to distinctly different levels which could be attributed to the three different coatings and their relative affinity for leachate components. The increase in aqueous concentration over background of Zn, Ti, and Ag was also observed during the method validation mass balance (2.0, 3.3, and 7.5 mg/L, respectively).

Figure 2 compares 30-day and background concentrations for the three metals in fractions less than 1500 nm. With the exception of Ag in Leachate E and TiO₂ in Leachates C and D, it was observed that there was a statistically significant increase

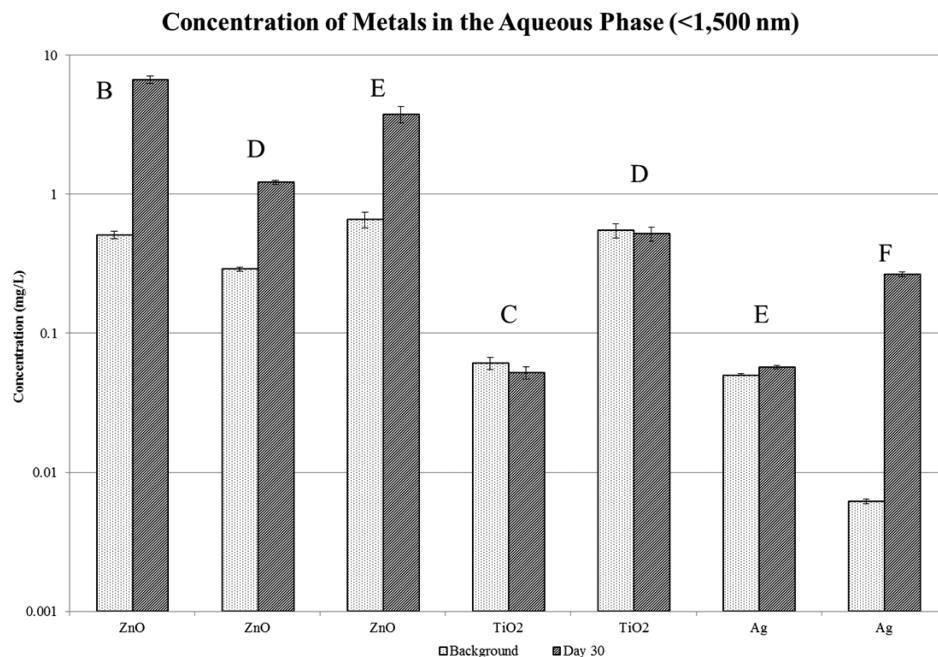


Figure 2. Comparison of metals concentrations in the aqueous phase before and after the addition of NPs (size fraction < 1500 nm) (middle-aged leachate: D,E; mature leachate: B,C,F).

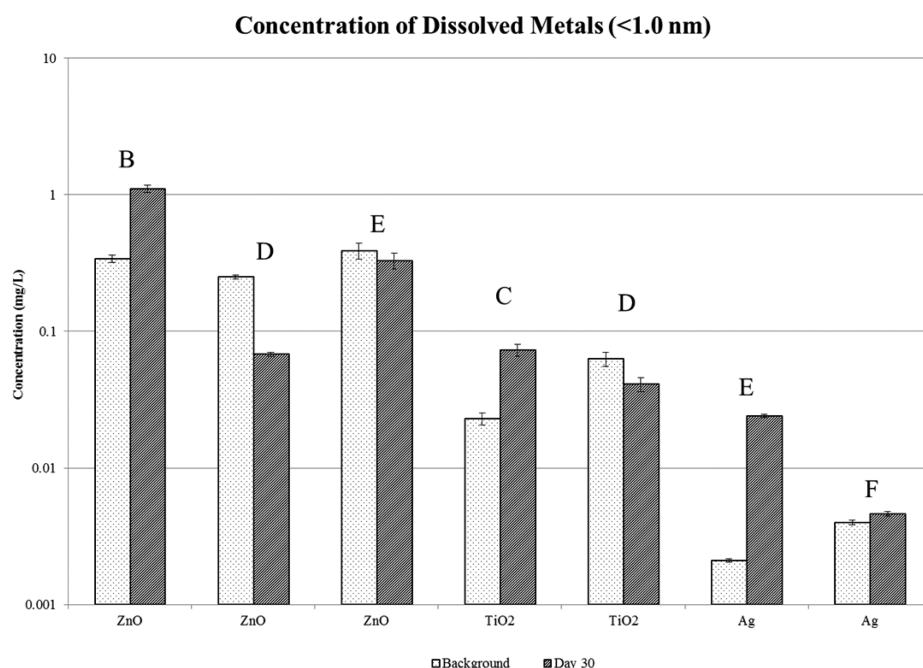


Figure 3. Comparison of dissolved metals concentrations before and after the addition of NPs (size fraction < 1.0 nm) (middle-aged leachate: D,E; mature leachate: B,C,F).

in the concentration of metals in this fraction, relative to background concentrations, again due to dispersion of NPs. Although an increase in TiO₂ concentration in the fraction <1500 nm was not observed in Leachates C and D, an increase in the unfiltered aqueous samples was measured in both the mass recovery tests (Table 1) and the 30-day sample (Figure 1) for Leachate C.

It has been reported that the presence of DOM increases the stability of both hydrophilic and hydrophobic NPs.^{25,40,43–46} DOM appears to interact with coated NPs, changing wetting properties of the coating and promoting NP dispersion.

Therefore, tested leachates with HA concentrations ranging from 300 to over 6500 mg/L would be expected to affect the dispersibility of the NPs. Age differences in leachates did not seem to affect the behavior of NPs. The agglomeration and resulting increase in Zn, Ti, and Ag concentrations in the aqueous fraction (Figure 1) may also be promoted by reactor stirring and the destabilization of HA-coated particles at the high leachate ionic strength.^{25,46–48} HRTEM images suggest that ZnO NPs were embedded in leachate solids matrices after addition to leachate samples (Figure S4).⁴⁹ Dynamic light scattering, atomic force microscopy data, and HRTEM⁴⁹ also

revealed that dispersed ZnO NPs tended to agglomerate in leachate.

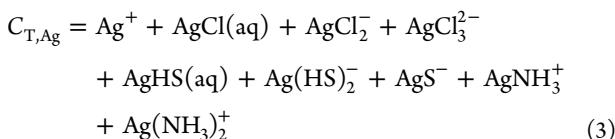
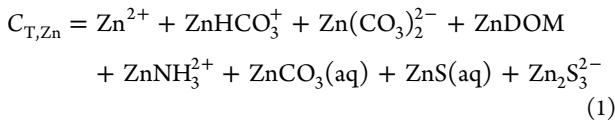
Due to the size of added NPs, any metals found in the dissolved fraction (<1.0 nm) above background concentration must have dissociated from NPs. The changes in the dissolved fraction were inconsistent, as shown in Figure 3. For example, Zn increased by 230% in leachate B, decreased by 73% in Leachate D, and remained relatively the same in Leachate E. Ti increased by 220% in Leachate C but decreased by 35% in Leachate D. Ag was observed to increase by an order of magnitude in Leachate E and by only 15% in Leachate F. The increases were statistically significant (*t* test comparison of means; $\alpha = 0.05$), but they were small in magnitude (less than 2% of the mass of NP added).

Dissolution of metals from NPs is dependent on the stability of the NP, the quality of the NP coating, particle aspect ratio, matrix characteristics, and NP size. NP size was observed in HRTEM images, e.g., Figures S1–S3, to vary from particle to particle, perhaps accounting for inconsistent dissolved metal results.⁴⁹ However, even the minimal increase in the concentration of dissolved Ti in Leachate C was surprising, since TiO_2 is relatively stable at pH values of tested leachates.⁵⁰ Likewise, oxidative dissolution of Ag NPs under strictly anaerobic conditions maintained in test reactors would not be expected; however, some dissolution was observed in Leachate E.

Speciation of Dissolved Metals in Landfill Leachate.

The chemical speciation of dissolved Zn, Ti, and Ag in Leachates B–F was modeled using input values summarized in Table 1 (leachate characteristics) and Figure 3 (concentration of metals in the fractions less than 1.0 nm after 30 days). The input values yielded chemical speciation data that were used to determine the form in which the dissolved metals take in leachate and the percentage of the dissolved metals present in their free ionic state (i.e., Zn^{2+} , Ti^{4+} , and Ag^+). Given the complexity of leachates, it is not possible to identify and measure all contaminants present; therefore, this modeling has clear limitations. Sensitivity analysis was performed on the unmeasured anions expected to have greatest effect on tested metals, chloride and sulfide. Historical data (unpublished) revealed that the sulfide concentrations in some of the tested leachates ranged from 0.33 $\mu g/L$ to 80 $\mu g/L$; this range was used in a sensitivity analysis for sulfide, while keeping other constituent constant. Additionally, chloride concentrations (unpublished) for middle-aged and mature leachate ranged from 2240 mg/L to 3800 mg/L and 213 mg/L to 1300 mg/L , respectively.

The chemical species potentially present in leachate which would be expected to affect metals in aqueous phase are summarized in eqs 1–3.



Chemical speciation detailed results are provided in Supporting Information (Tables S1–6). The results from the sensitivity analyses suggest that these ions would not control Zn or Ti speciation. Zn is likely predominately associated with DOM (e.g., HA), carbonate ($ZnCO_3$ (aq)), and bicarbonate ($ZnHCO_3^+$), and is also present as free ionic Zn^{2+} . Speciation modeling showed that less than 1% of the dissolved Zn in Leachates B–D was present as free ionic Zn^{2+} . The remaining species shown in eq 1 would likely make up less than 2% of the total concentration of dissolved Zn (Leachates B, C, and D: 0.827, 0.061, and 0.06 mg/L of Zn^{2+} , respectively). The results from the sensitivity analysis on chloride and sulfide concentration were in agreement with species primarily associated with Zn (Figures S10–13). Any dissolved Ti would likely be present solely as $Ti(OH)_4^-$, as shown in eq 2, regardless of leachate characteristics.

If sulfide concentrations were less than 10 $\mu g/L$ and 5 $\mu g/L$ in Leachates E and F, respectively, Ag would be predominately associated with ammonia ($Ag(NH_3)_2^+$) and chloride ($AgCl_2^-$ and $AgCl$ (aq)), and also present as free ionic Ag^+ . Less than 1% (0.12 $\mu g/L$ and 0.026 $\mu g/L$) of the dissolved Ag present in Leachates E and F, respectively, would be free Ag^+ . At sulfide concentrations greater than 10 $\mu g/L$ and 5 $\mu g/L$ in Leachates E and F, respectively, Ag would be predominately associated with hydrogen sulfide ($AgHS$ (aq)) and sulfide (AgS^-), since the pH of the studied leachates were approximately 7.5 S.U. (H_2S $pK_a = 7.0$), and free Ag^+ would be absent in Leachates E and F.

The sensitivity analysis of chloride indicated that chloride would have minimal effect on the speciation of Ag^+ . It was predicted that increased concentrations (~1000 mg/L) would yield a decrease in the Ag^+ . Further analysis revealed that chloride had no effect on the availability of Ag^+ and sulfide and ammonia controls the chemical speciation of Ag (Figures S13–14).

Effect of Coated Nanoparticles on Biological Processes. The BOD_5 of leachate after exposure to varying concentrations of NPs was analyzed over time; the differences between the control and test reactors were evaluated using the standard Student *t* test ($\alpha = 0.05$) for individual BOD_5 results. Likewise, BMPs in test reactors were compared to the control reactors. The BOD_5 was observed to decline over time, presumably due to the conversion of organic matter to methane and carbon dioxide under the reactor anaerobic conditions. The disappearance of BOD_5 over time and the generation of methane during BMP tests were both found to follow first-order kinetics (see Supporting Information Figures S9–24) which allowed a comparison of first-order rate constants for test reactors with controls. The statistical significance tests for both BOD_5 and BMP studies relative to the controls are summarized in Table S-5.

Differences in BOD_5 and first-order rate constants between test reactors and controls were not statistically significant, as the calculated Student *t*-value for each reactor relative to the control fell within the hypothesis ($\alpha = 0.05$). These results suggest that added NP did not change the ability for microorganisms to break down organic matter aerobically. High dilutions necessary for BOD_5 testing of leachate may have masked inhibition; however, the similarity of results for BOD_5 removed over time in reactors (as measured by first-order rate constants) supports a lack of inhibition. The GGA control had a BOD_5 value of 154 mg/L , while the BOD_5 values of GGA solutions exposed to 100 mg/L of ZnO , TiO_2 , and Ag NPs were 144 mg/L , 142 mg/L , and 1.2 mg/L , respectively. Results

showed that ZnO and TiO₂ did not affect the biochemical oxidation of organic matter relative to the control; conversely, Ag inhibited oxygen consumption in the GGA BOD₅ test in the absence of leachate constituents.

Differences between test reactors and control BMPs and the first-order rate constants for methane generation were not statistically significant, as the calculated Student *t*-value fell within the hypothesis ($\alpha = 0.05$), suggesting that the NPs added did not affect the ability for microorganisms to generate methane. A lag in the gas production for Leachate C exposed to TiO₂ was observed but the cumulative gas production was higher than control reactor. Therefore, it can be concluded that ZnO, TiO₂, and Ag NPs, added to leachate, did not inhibit either aerobic or anaerobic processes.

Dissolved Zn²⁺ in the environment has been identified to be toxic, provided it is bioavailable. ZnO NP toxicity has been observed in *Escherichia coli* and endogenous respiration and BOD biodegradation in wastewater treatment at concentrations between 500 mg/L and 800 mg/L.^{51,52} Additionally, Mu and Chen⁵³ reported that toxicity in anaerobic digestion was observed at concentrations of 11.6 mg/L and 17.6 mg/L of Zn²⁺. The Zn concentrations quantified in our study were significantly lower in comparison to the referenced studies, which supports the lack of inhibitory effects observed in BOD₅ and BMP tests.

It has been suggested that if Ag is bound to a ligand the toxicity of Ag NPs to aquatic organisms can be suppressed.⁵⁴ The antibacterial properties of Ag NPs have also been shown to decrease in the presence of dissolved natural organic matter and divalent ions.^{55,56} A study by Posgai et al.⁵⁷ showed that Ag NP toxicity was reversed through the chelation of silver ions that were released from the added Ag NPs. The chemical speciation model predicted that Ag was predominately chelated with either sulfide or ammonia, which may explain the lack of inhibition that was found in the BOD₅ and BMP leachate studies, while toxicity was observed in the GGA solution in the absence of these compounds.

TiO₂ NPs have been found to cause oxidative stress in organisms from the formation of reactive oxygen species (ROS). Aquatic toxicology studies on freshwater algae showed little to no toxicity in the presence of TiO₂ NPs. Exposing freshwater algae to TiO₂ NPs in the presence of UV irradiation caused the formation of ROS, which inhibited their growth.⁵⁸ Toxicology testing conducted on *Bacillus subtilis*, *Escherichia coli*, and *Vibria fischeri* at high concentration of TiO₂ (>2 mg/L) inhibited growth of these bacteria.^{58,59} For example, the growth of *Escherichia coli* was reduced by 72% when exposed to 5 g/L of TiO₂ NPs. Lin et al.⁶⁰ observed a decrease in inhibitory effects of TiO₂ on algal growth in the presence of HA due to the formation of TiO₂-HA complexes. HA can also decrease the intracellular ROS generation at concentrations greater than 5 mg/L. Therefore, the lack of inhibition in our studies can be explained by the low concentrations of aqueous Ti, high concentrations of HA in leachate, and the absence of UV irradiation.

In summary, NP characterization, leachate size fractionation, BOD₅ and BMP tests, and chemical speciation modeling provided insight into the mobility of NPs in landfill leachate and the effects on landfill biological processes. Increased aqueous phase concentrations support dispersibility and dissolution of the added NPs due to interaction with leachate components, stabilizing the NPs in the aqueous solution. However, the majority of the aqueous NPs aggregated and were

present as larger particles which might be retained in the solid waste as the leachate moves through the landfill. Due to the heterogeneity of landfill leachate and the variation in NP characteristics, it is challenging to predict the mobility of NPs in a landfill. Knowledge gaps exist regarding the mechanisms controlling the fate of NPs in landfills due to the lack of analytical techniques that can identify NPs in a complex heterogeneous matrix, and to variations in NP coating, size, and shape.

ASSOCIATED CONTENT

S Supporting Information

Details of HRTEM analysis, dissolved concentrations of metals less than 1.0 nm, chemical speciation and sensitivity analysis of dissolved metals, and figures showing BOD₅ and BMP result. This material is available free of charge via the Internet at <http://pubs.acs.org.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Ag, silver; BOD₅, five-day biochemical oxygen demand; BMP, biochemical methane potential; CH₄, methane; CO₂, carbon dioxide; COD, chemical oxygen demand; DOM, dissolved organic matter; HRTEM, high resolution transmission electron microscopy; HA, humic acid; ICP-OES, inductively coupled plasma-optical emission spectrum; MSW, municipal solid waste; NMs, nanomaterials; NPs, nanoparticles; Ti, titanium; TCD, thermal conductivity detector; HRTEM, high resolution transmission electron microscopy; TiO₂, titanium dioxide; ZnO, zinc oxide; Zn, zinc

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