FATE OF COATED NANOPARTICLES IN LANDFILL LEACHATE

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Introduction

Project Objectives

- This research seeks to understand the fate of NMs within waste environments by examining the interactions between NPs and landfill leachate components.
- Primary focus was on the effect of Zinc Oxide (ZnO), Titanium Dioxide (TiO_2), and Silver NPs (Ag) on:
  - Biological landfill processes
  - Solids aggregation
  - Chemical speciation of dissolved metals in leachate following the addition of nanoparticles (NPs)

Methodology

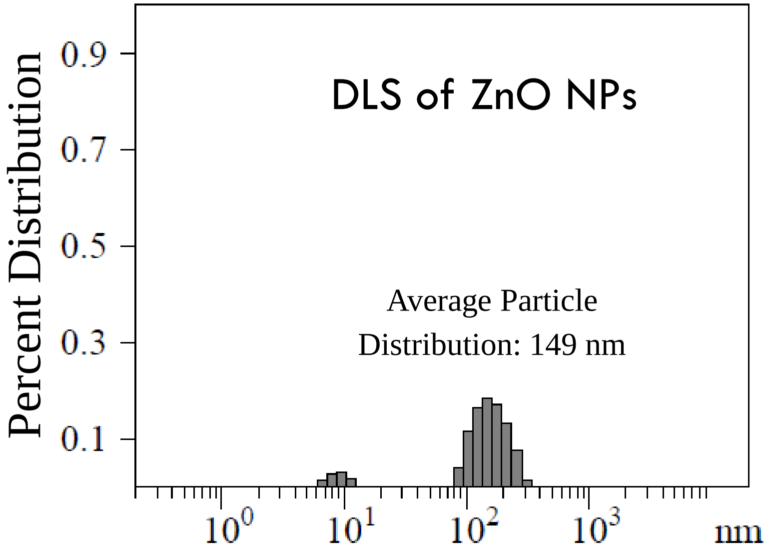
Leachate Collection and Chemical Characterization

- Middle-aged and mature leachate samples were collected and characterized from MSW landfills in Florida.
- All leachate samples were characterized for:
  - pH
  - Chemical and biochemical oxygen demand
  - Ammonia-nitrogen
  - Conductivity
  - Alkalinity
  - Heavy metals
  - Total suspended and dissolved solids
  - Dissolved humic acid concentration

All procedures followed Standard Methods for the Examination of Water and Wastewater.

Materials Used

- Coated Zinc Oxide (ZnO).
  - Triethoxycaprylylsilane
- Coated Titanium Dioxide (TiO_2).
  - Hydrated Silica and Dimethicone/Methicone Copolymer and Aluminum Hydroxide.
- Coated Silver (Ag).
  - Polyvinylpyrrolidone (PVP) coated Ag nanoparticles



ZnO NPs

Leachate Exposed to Coated NPs

- Leachate was exposed to varying concentrations of coated NPs.
  - 100 µg/L NPs
  - 1.0 mg/L NPs
  - 100 mg/L NPs
- Continuously stirred (~24°C)
- Control reactor was treated in the identical manner without NPs.

Materials Characterizations

- HRTEM: Particle size, crystallinity and particle morphology,
- HRTEM - Selected Area Electron Diffraction (SAED) for identification of crystallinity and elemental analysis (composition)
- DLS to understand size and size distribution of the particles in solution,
- UV-Vis spectroscopy for absorption measurements.
- Fluorescence spectroscopy for detailed investigation of the emission properties of coated ZnO particles and for understanding their interaction with leachate components,
- FT-IR spectroscopy for understanding the interaction of coated ZnO NPs with the leachate components,
- AFM for the imaging of ZnO NPs in leachate components.

Effect of Coated NPs on Biological Processes

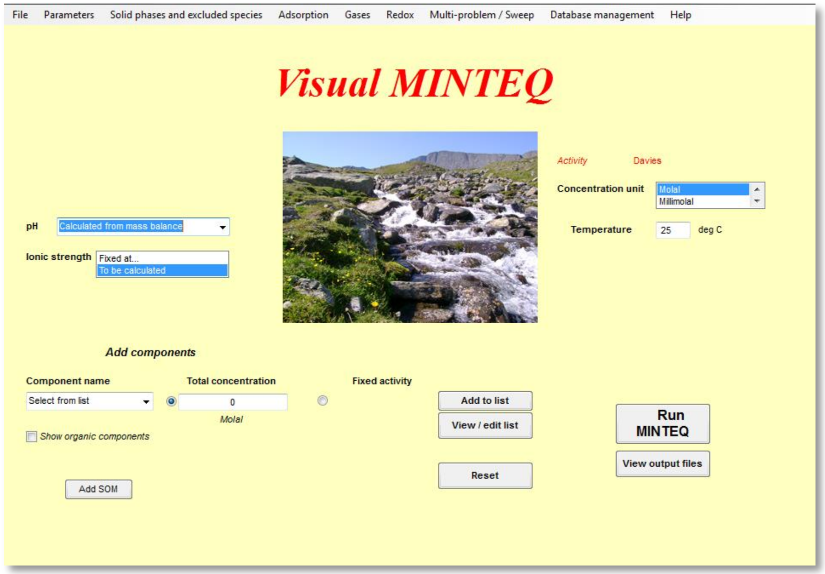
- Biochemical Oxygen Demand (BOD_5) was performed following standard methods 5120B.
- Biochemical Methane Potential (BMP) was performed following ASTM method E2170.

Size Fractionation of Leachate Samples Exposed to Coated NPs

- Size fractionation was used to determine the effect of solids aggregation on the fate of NPs and to quantify the concentration of dissolved metal ions in each fraction.
  - 1.0-nm (1000 NWML regenerated cellulose) filter.
- Concentration of metals (Zn, Ag, Ti) in each size fraction was quantified using Inductively Coupled Plasma-Optical Emission Spectrum.

Chemical Speciation of Dissolved Metals using Visual MINTEQ

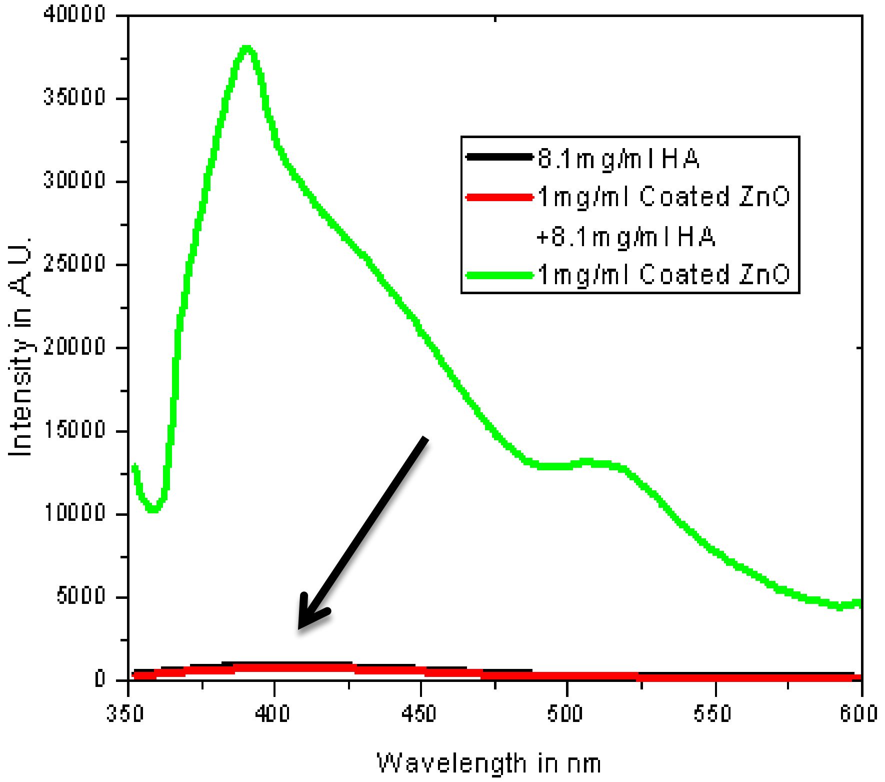
- Chemical speciation of metals in leachate is an important component in understanding the toxicity, mobility, and bioavailability of these metals in the environment.
- Estimate the chemical species and equilibrium mass distribution of dissolved metals found in leachate using Visual MINTEQ



Findings

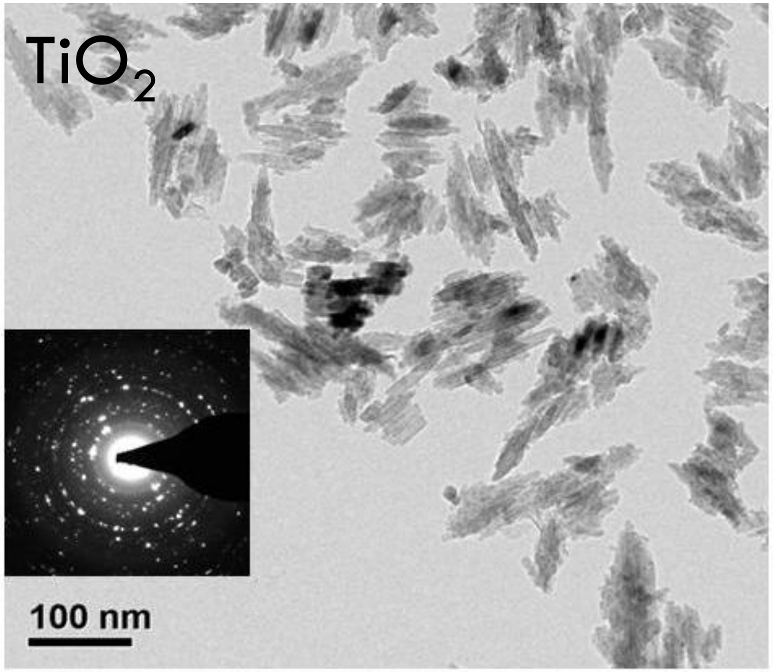
NP Dispersibility

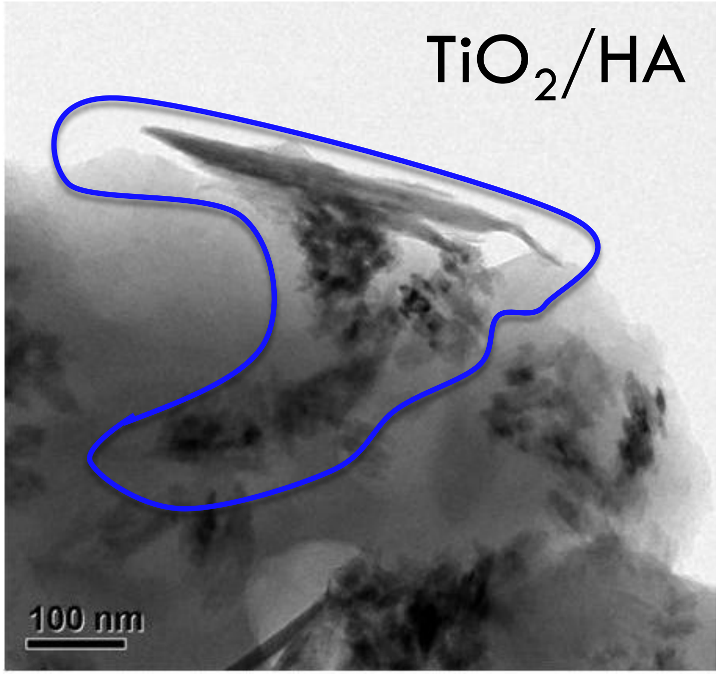
- Humic acids (HA) greatly increased the dispersibility of the coated ZnO NPs, which can be attributed to over-coating of NP surface by HA through hydrophobic-hydrophobic interaction.
- Fourier Transform Infrared (FT-IR) spectroscopy and fluorescence characterization data confirmed that HA was adsorbed onto coated ZnO NPs, increasing their wettability.



NP Interaction with Humic Acids

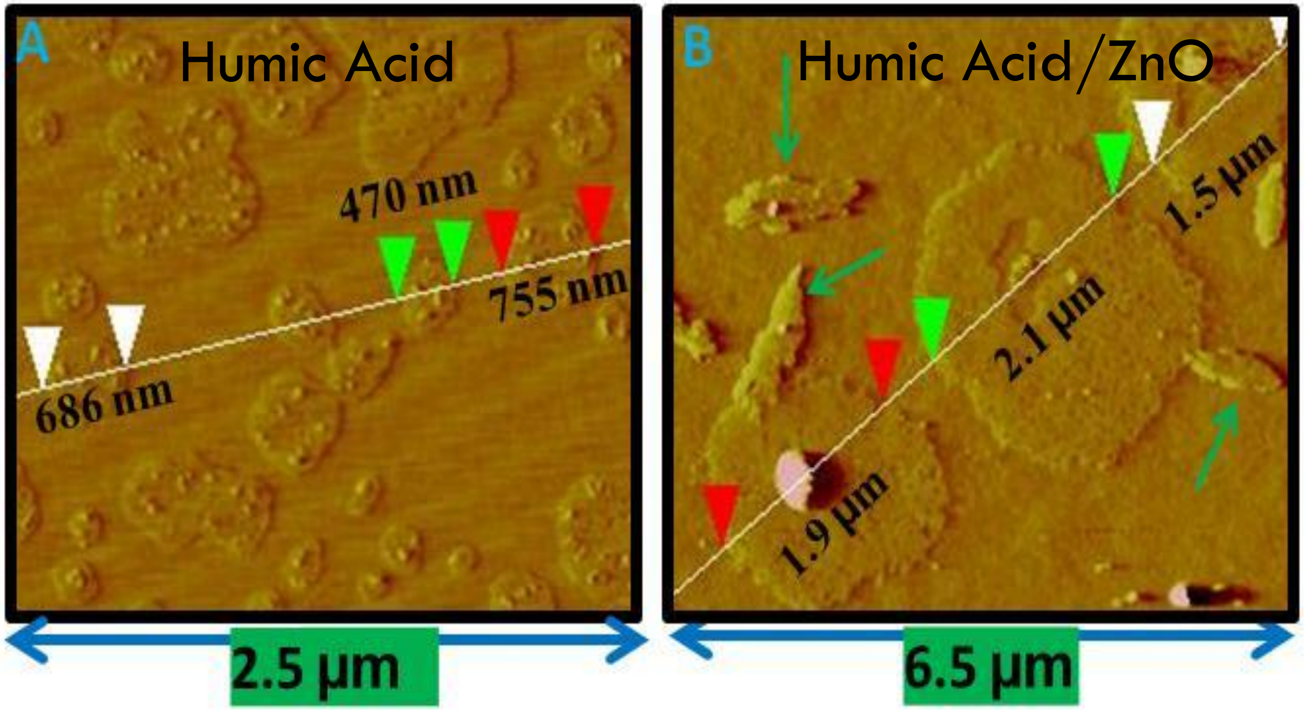
- High Resolution Transmission Electron Microscopy images suggested that ZnO NPs were embedded in leachate matrices after addition to leachate samples. TiO_2 was observed embedded in purchased HA.



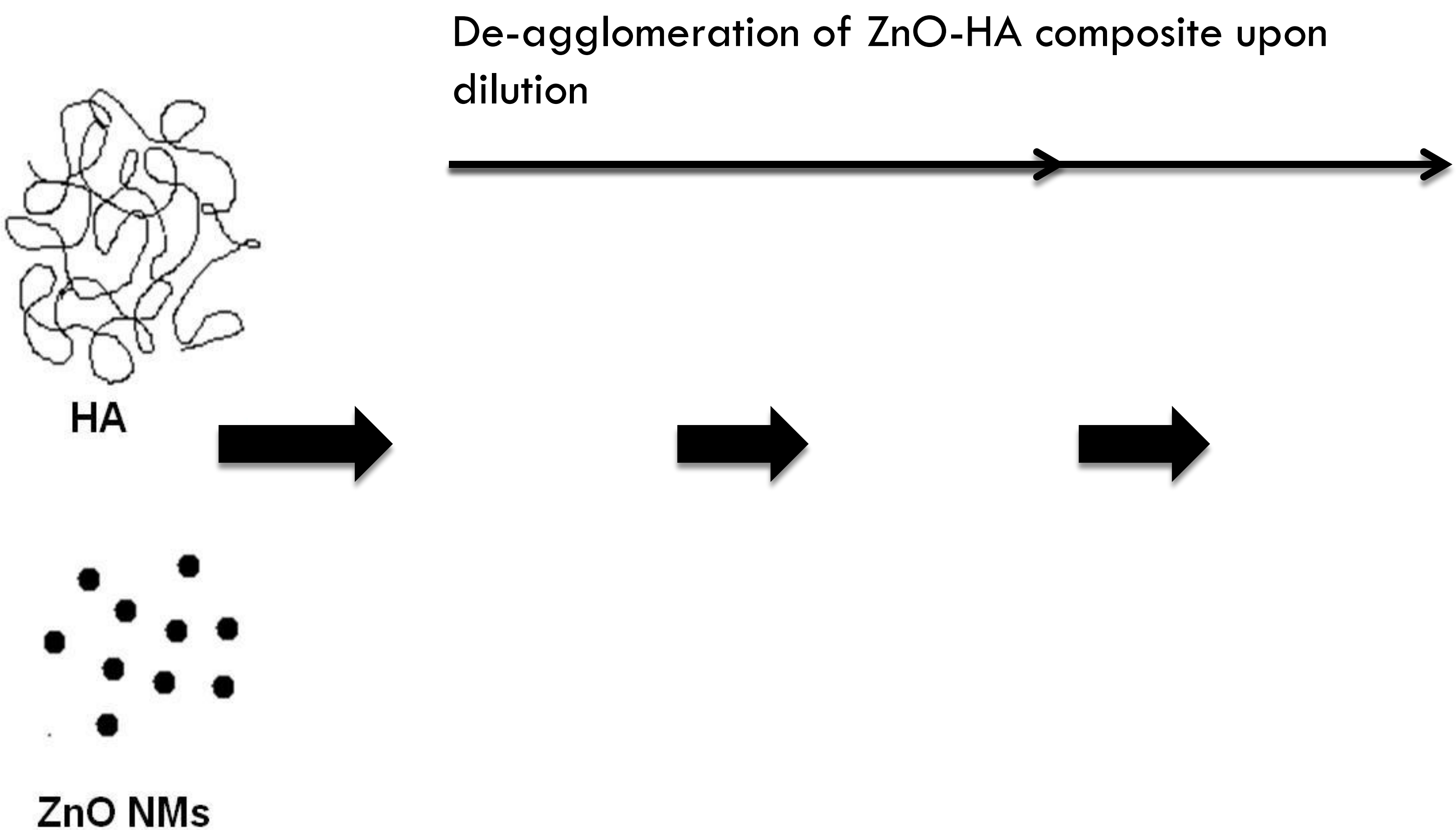


NP Agglomeration in Leachate

- Dynamic Light Scattering and Atomic Force Microscopy data revealed that dispersed ZnO NPs tended to agglomerate in leachate. Fractionation studies also showed that ZnO as well as Ag NPs agglomerated in leachate.

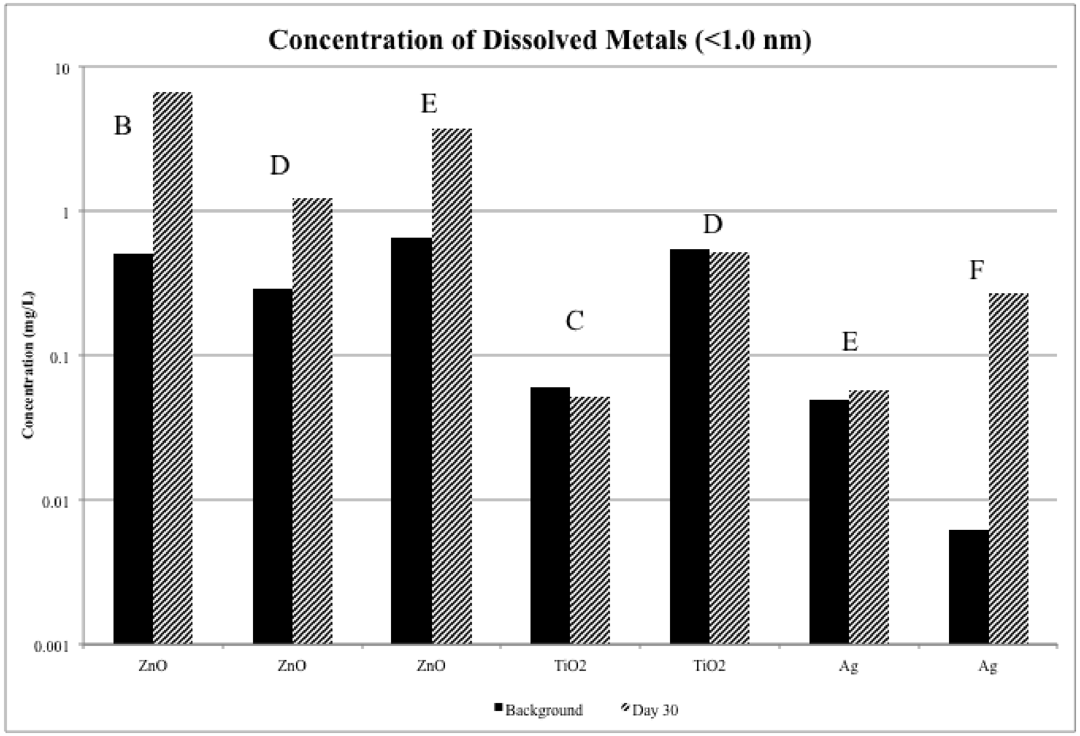


Agglomeration of ZnO-HA Composite and De-Agglomeration Upon Dilution



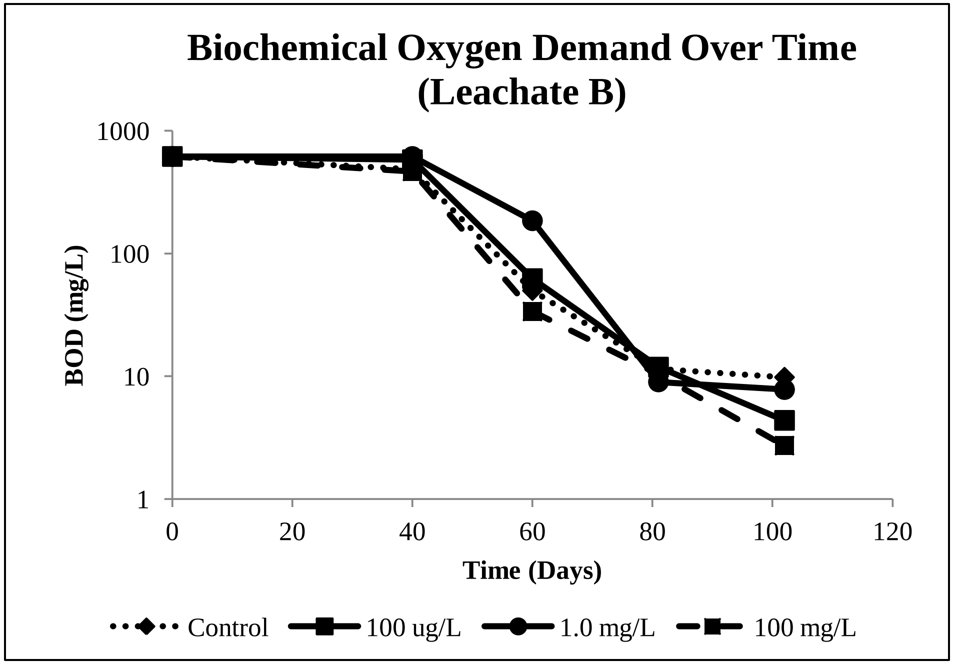
NP Dissociation in Leachate

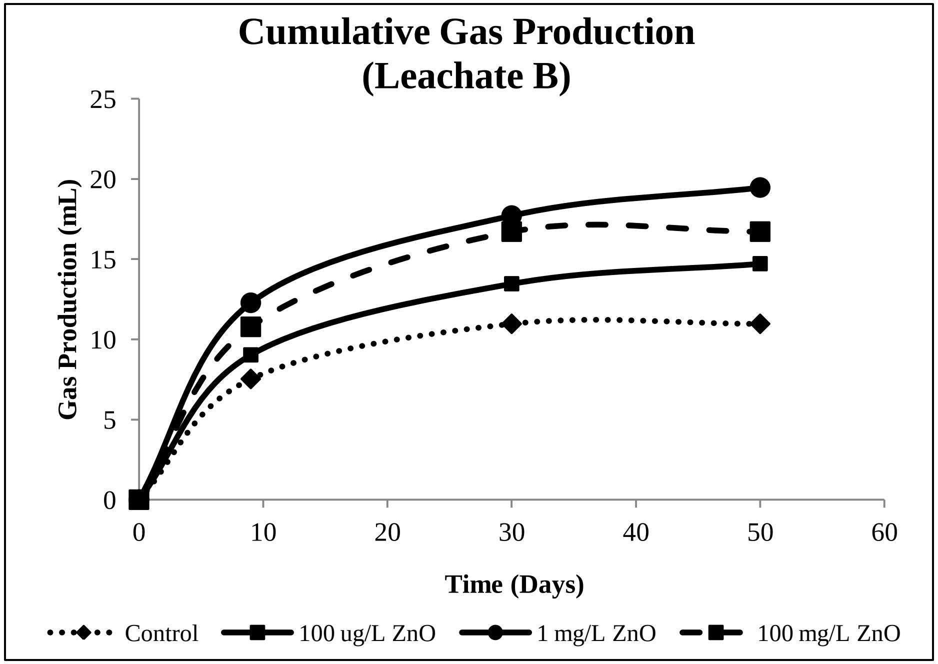
- An increase in the dissolved concentration of all tested NPs was observed in some leachates, which supports dissociation of these NPs, however this fate accounted for less than 1% of the mass of NP added.



Biological Effects

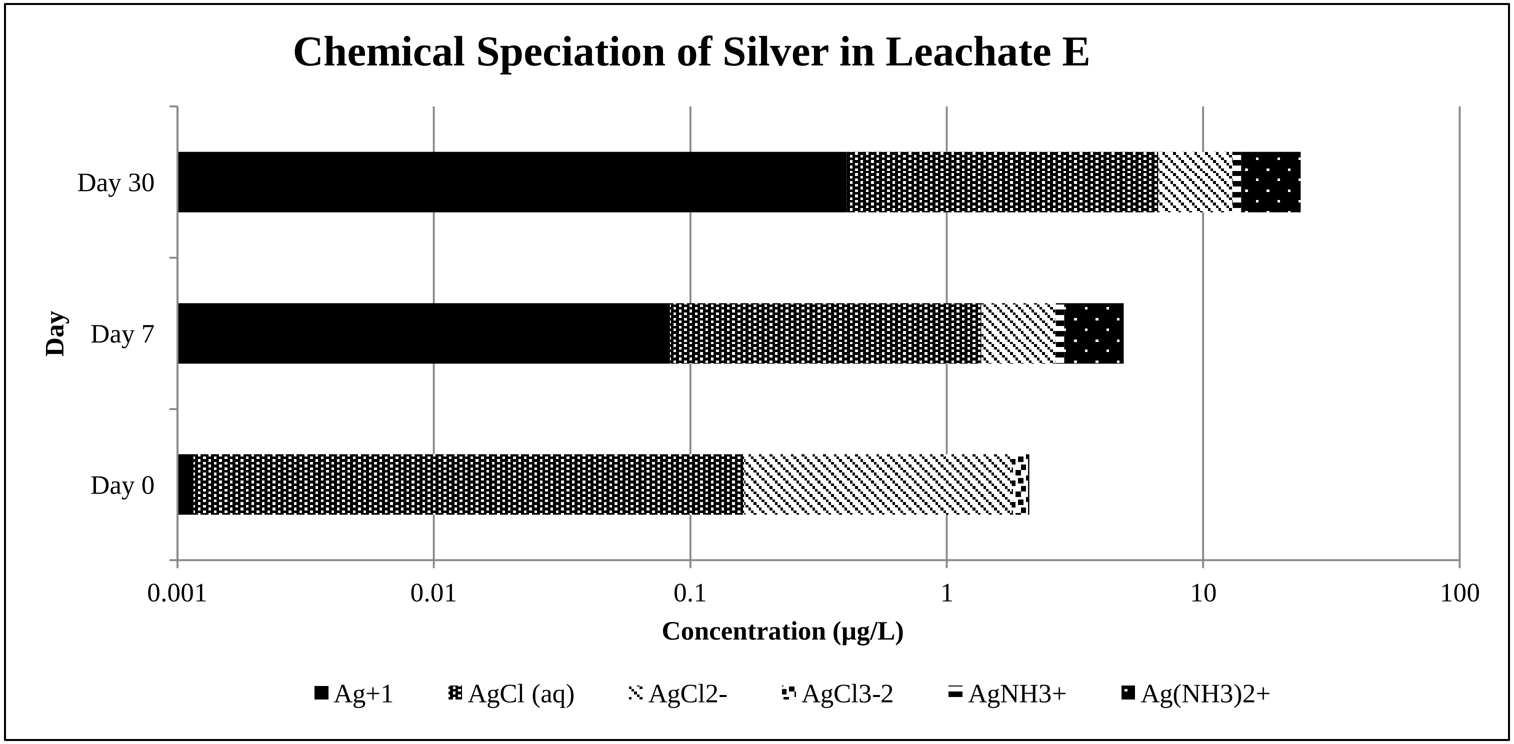
- ZnO, Ag, and TiO_2 NPs did not affect biological processes when added to middle-aged and mature leachate as measured by Biochemical Oxygen Demand and Biological Methane Production tests.





Metal Speciation Modeling

- MINTEQ models showed that dissolved Zn, Ag, and Ti in leachate were associated with HA, NH_3/Cl, and hydroxide, respectively. Low concentrations of free ions were predicted.



Conclusions

Conclusions: Summary

- Insight into the mobility of NPs in landfills
  - Aggregation may prevent movement through traditional containment systems
  - Transported out of the landfill in leachate due to increased dispersability
- Absence of inhibitory effects on landfill processes
  - Biological treatment of leachate should be unaffected by the presence of NPs
  - Bioavailability of dissolved metals was not affected by the added NPs due to the affinity of dissolved metals for DOM (HA), NH_3/Cl, and hydroxide.
- Challenging to predict overall mobility of NMs in a landfill due to the complexity of landfill leachate and the utilization of different NM coatings.

Questions

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