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Groundwater under Hope College's Campus: Suspended Load Characterization

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Introduction

In the past few decades, engineered nanoparticles (ENPs), or nanomaterials (ENMs), have become increasingly explored in the realm of geochemistry due to their increase in use in production and environmental remediation (Montaña et al, 2014);(Peijnenburg et al, 2015)[a]. Most ongoing research has observed the fate of ENPs in the natural environment. This involves monitoring their movement through a system and categorizing their interactions with surrounding sediments based on environmental factors such as pH and ionic strength, and the presence of *naturally* occurring nanoparticles (NNPs) (Peijnenburg et al, 2015)[b]. ENPs are introduced to groundwater and/or sediment in several different ways including accidental plant spills or purposeful implementation of ENPs for environmental or water cleanup (Montaña et al, 2014). Urban groundwater has received considerable study over the past 30 years due to contamination and subsequent remediation. However, less attention has been paid to the *solid suspended load* in urban groundwater which could include fractions of anthropogenic ENPs. The goal of this research project was to characterize, or quantity, the very-fine, near-nano (0.2-0.7 µm) fraction of suspended (and suspendable) solids present in shallow (3-7 m below grade) urban groundwater aquifer under Hope College's Campus.

Figure 1. This is a demonstration of variation in well settling between well sampling localities and suspended sediment composition. Some photography was used to capture the shift in water clarity as the particles settled out of suspension during a 60 minute period. Notes that what is in suspension in the samples may or may not be reflective of what particles are suspended within the well due to the potential for disruption when samples are collected.

Methods

Materials:
11 wells and 1 drainage ditch were sampled from in a 1 km^2 area. The land use of the areas included residential and lawn (2 wells), street (2), sidewalk (1), parking lot (1), former industrial site (1), storm surge basin on former industrial site (2), municipal drainage ditch (1), and surface drainage ditch runoff (1) sites. Wells were constructed from 10 m schedule 40 PVC pipe with a mesh screen, and well depth ranged from 3 and 7 m deep.

Timed Settling Procedure:
250-mL of each sample was allowed to settle for a total of 60 minutes. For the first 30 minutes, every 2 minutes a sample of 7-mL of the suspension at the top 2 cm were drawn and placed into a MicroLab vial. For the remaining 30 minutes a samples was taken every 5 minutes, yielding a total of 22 samples, with two taken at the 60 minutes mark so that one could be centrifuged.

Modified Navier-Stokes Equation:
The Navier-Stokes equation was adapted to obtain a relationship between time and particle size. The first approximation used was a simple Stokes settling equation, and this provided insight to the general trend of particle size with settling time. An intermediate Navier-Stokes adaptation was used as another approximation, with variables to find particle size dependent on fluid density, suspended particle density, fluid viscosity, settling velocity, and time. An adaptation of Ferguson and Church's universal equation for grain-settling velocity was used, where the equation was solved for particle size rather than velocity, and velocity was put into terms of settling distance per unit time. This is shown below in Figure 2, where particle diameter begins at just over 4 microns and by about a half hour suspended particles are down to the nano-range for most minerals, and that happens by about 10-15 minutes for the iron phase.

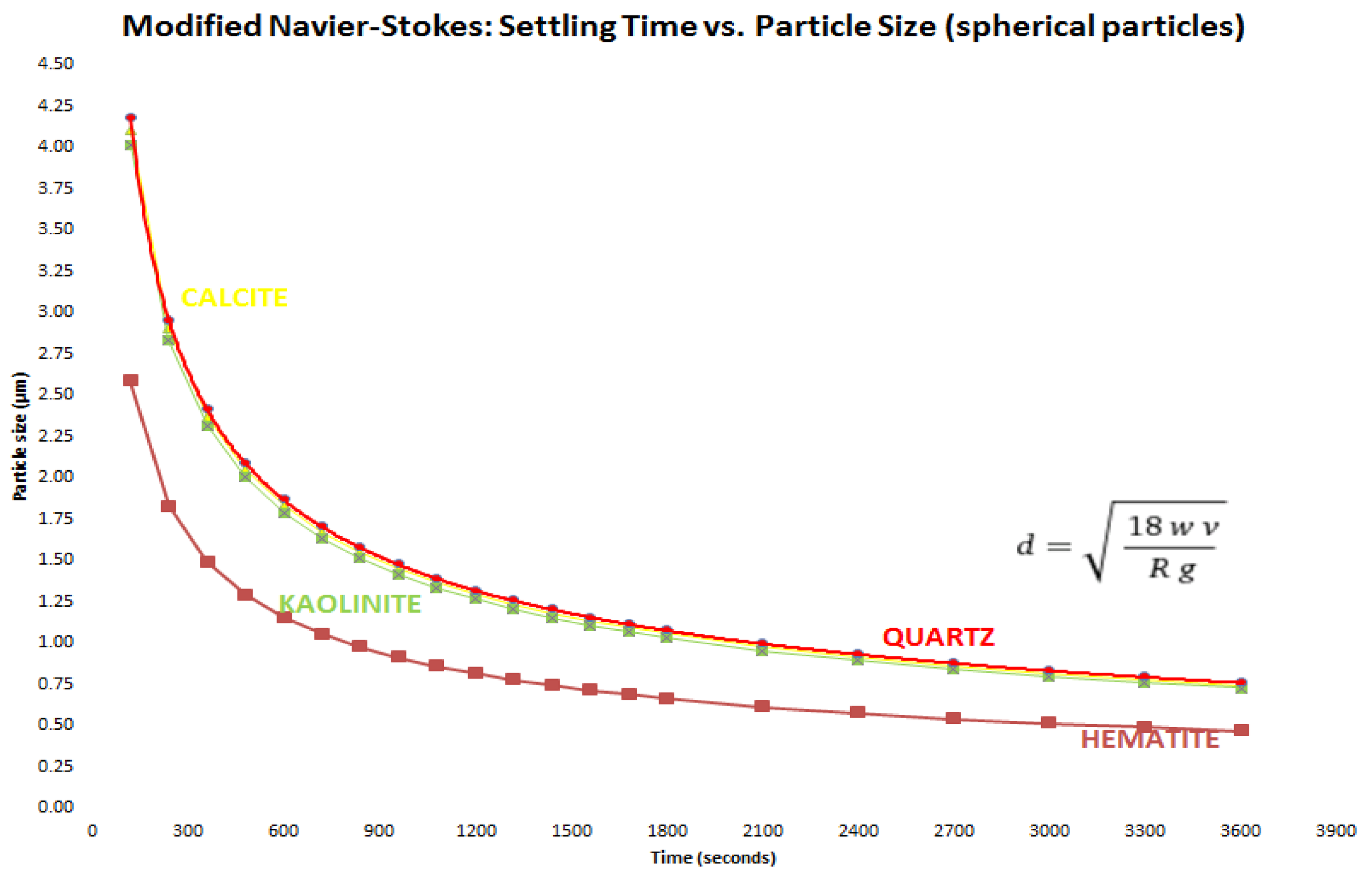


Figure 2. A relatively quick way of estimating particle size in the suspensions was to apply the Modified Navier-Stokes Equation to common natural mineral particles. The density of the non-iron particles is similar enough to have very little effect on settling time. These preliminary calculations were for sphere particles, which suggests that settling differences are driven more by particle shape than density.

Results

Dynamic Light Scattering (DLS) done through Oak Ridge National Laboratory on the four focus wells. These results are show below, with the surge basin particles around 1 micron, compared to the campus lawn and street wells that are well below that to nearly 400 nanometers.

Well	Average Particle Diameter (nm)	STDEV (±)
Residential Lawn (11)	848	25
Campus Lawn (14)	439	5
Street (17)	589	16
Surge Basin (34)	1076	31

Table 1. Measurements of wells 11, 14, 17, and 34 using DLS was used to determine average particle diameter and standard deviation.

The spectrophotometry data collected from MicroLab was combine with the Modified Navier- Stoke equation to estimate the particle concentrations of the particle sizes in each of the wells. These data are shown in Figure 4, where different land uses present different suspension concentrations and particle distributions. This was used to compare the land uses of each well and the particle sizes in suspension at any given time. From this graph, the four focus wells were selected because of the range in particle sizes they demonstrated between various land uses. The four focus wells are residential lawn (well 11), campus lawn (14), street (17), and surge basin (34).

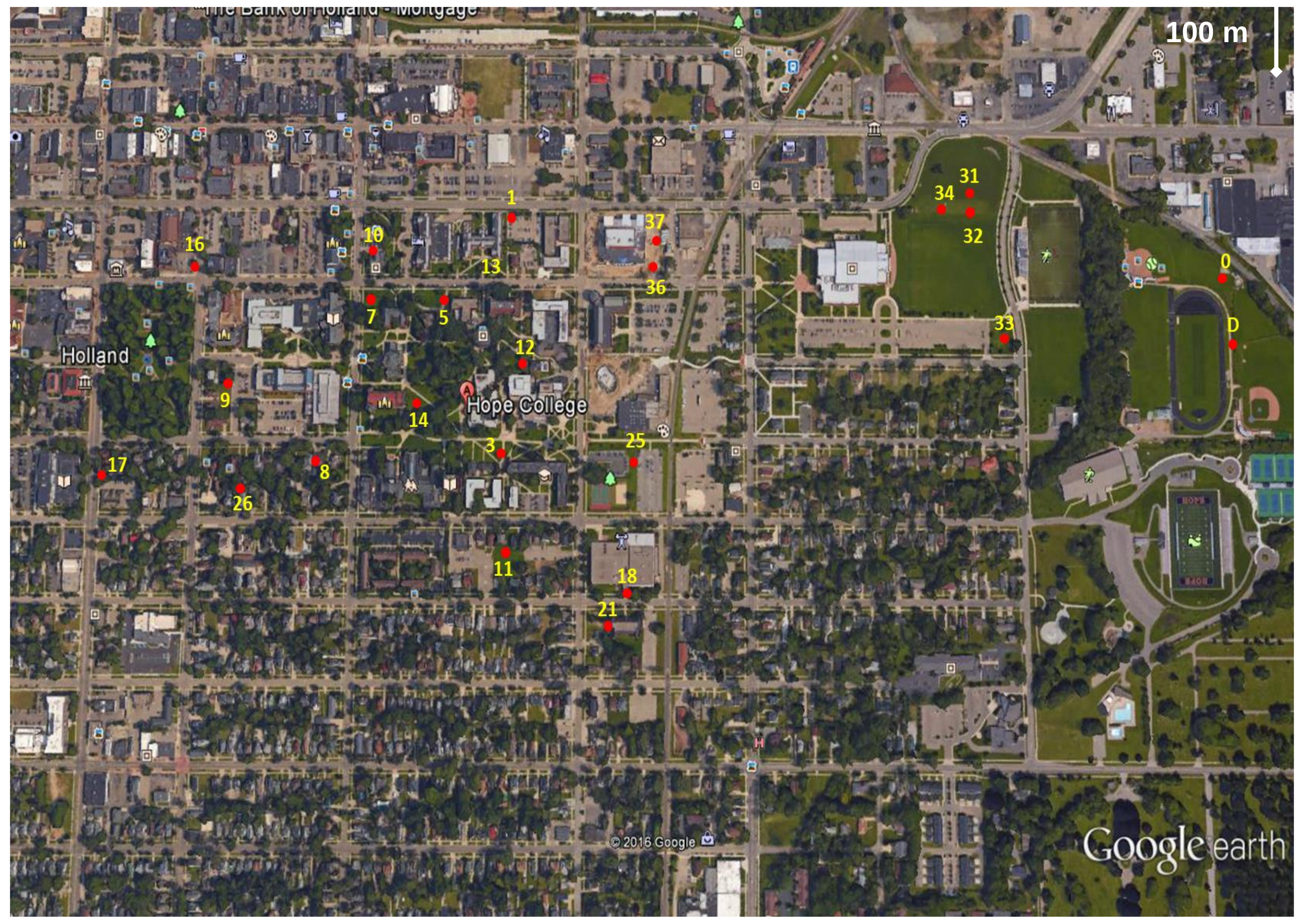


Figure 3. Aerial view of Hope College campus highlighting the 25 well localities characterized within a 1 km^2 area. The five images above are examples of some of the land use types that were sampled from. Moving from left to right the localities represent streets, sidewalks, surge basins, lawns, and parking lots for sampling sites.

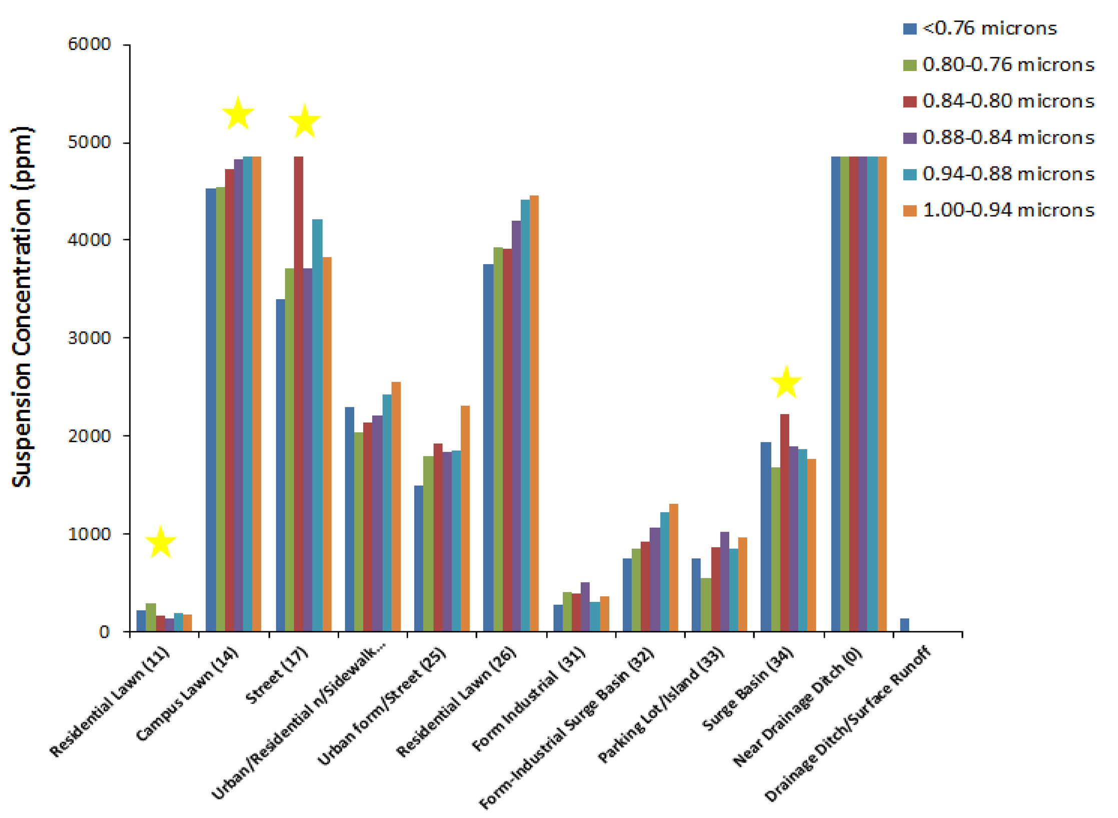
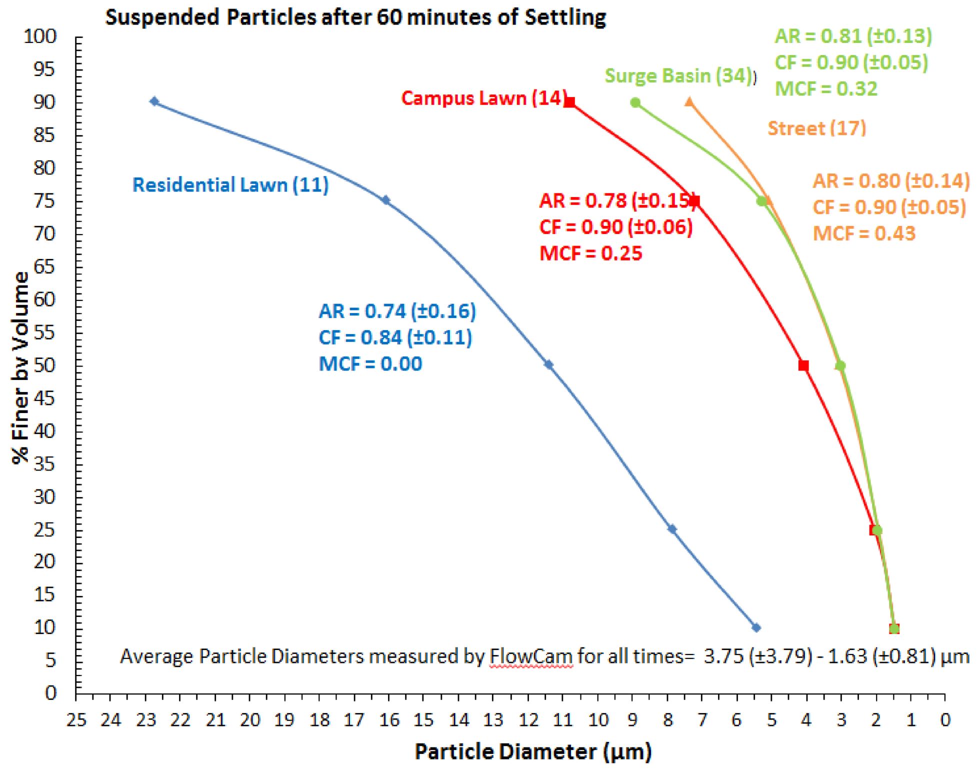


Figure 4. The spectroscopy data combined with the Modified Navier-Stokes equation provides insight to the concentrations of particle sizes in all of the wells sampled from. The highest concentrations are about 4900 ppm under a campus lawn, and lowest concentrations under a residential lawn and former industrial site

Using FlowCam images generated by Oak Ridge National Laboratory, a measurement of Percent (%) Finer by Volume was found for each sample. Figure 5 demonstrates this for the four focus wells. After 60 minutes of settling, the particles in suspension are not as well sorted as the other wells at this point. It can be observed that the surge basin and the street material comparatively show better sorting on particle size, with 10 volume 5 of the sample less than 1.4 microns diameter. FlowCam imaging also measures shape. The aspect ratio, circle fit, which is a measure of "sphericity,"and minimum circle fit were measure in the samples.

Figure 5. Percent (%) Finer by Volume measurements collected by FlowCam imaging . Shape measurements were also found for the four focus wells including aspect ratio (AR), circle fit (CF), and minimum circle fit (MCF). Note that the most angular particles are found in the residential lawn (11).



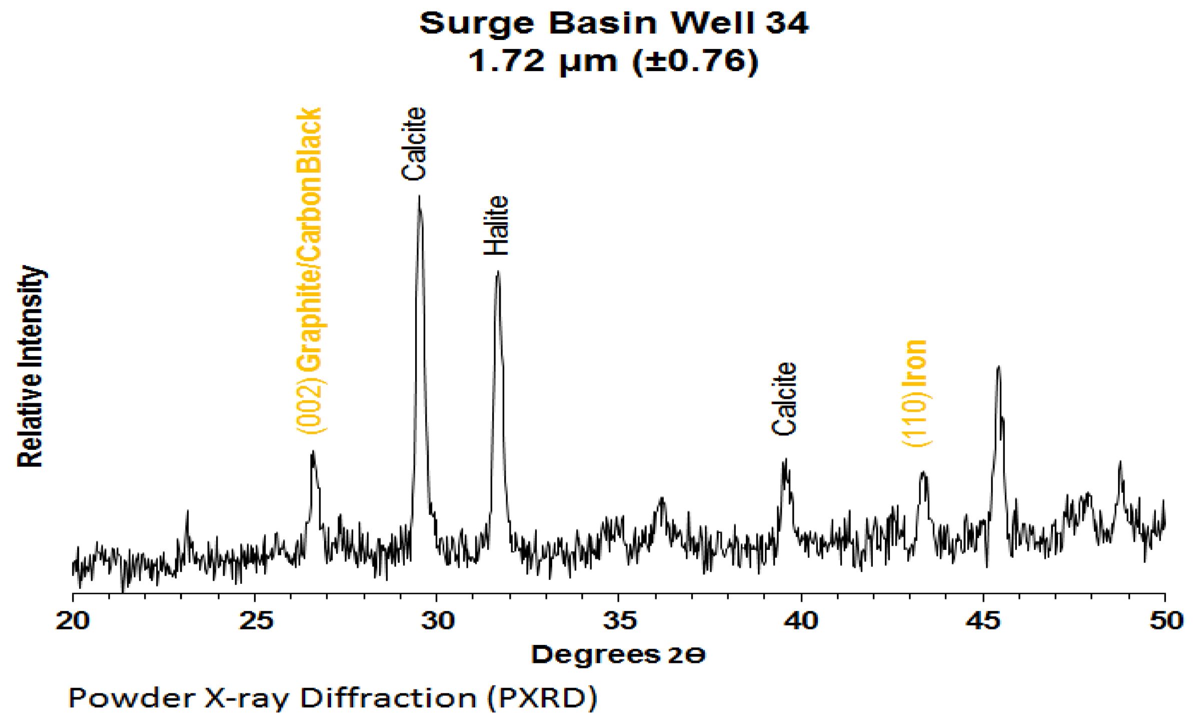


Figure 6. Measurements collected using PXRD show that both graphitized carbon black or graphite, reflector at 002, and iron , reflector at 110, appeared in the surge basin (34). The halite that appears in this sample is thought to be from the drying process in which the salt crystals would have been able to form.

Anthropogenic particles were found in both the surge basin and street samples using Powder X-Ray Diffraction (PXRD). It was clear that small amount of graphitized carbon black and graphite were found in these wells. Small amounts of metallic iron were also found in the surge basin, which could be linked to the industrial past of that locality. PXRD of the particles in the 63 micron fraction of these wells consisted of quartz, some feldspar, and clay.

The combination of the DLS and FlowCam measurements with the Modified Navier-Stokes equation allowed for comparison of the particle sizes and settling times. This aimed to create a model that could begin to predict settling time based upon the particle size and composition of particles in suspension. This relationship is shown below in Figure 7 with the wells and common minerals in groundwater.

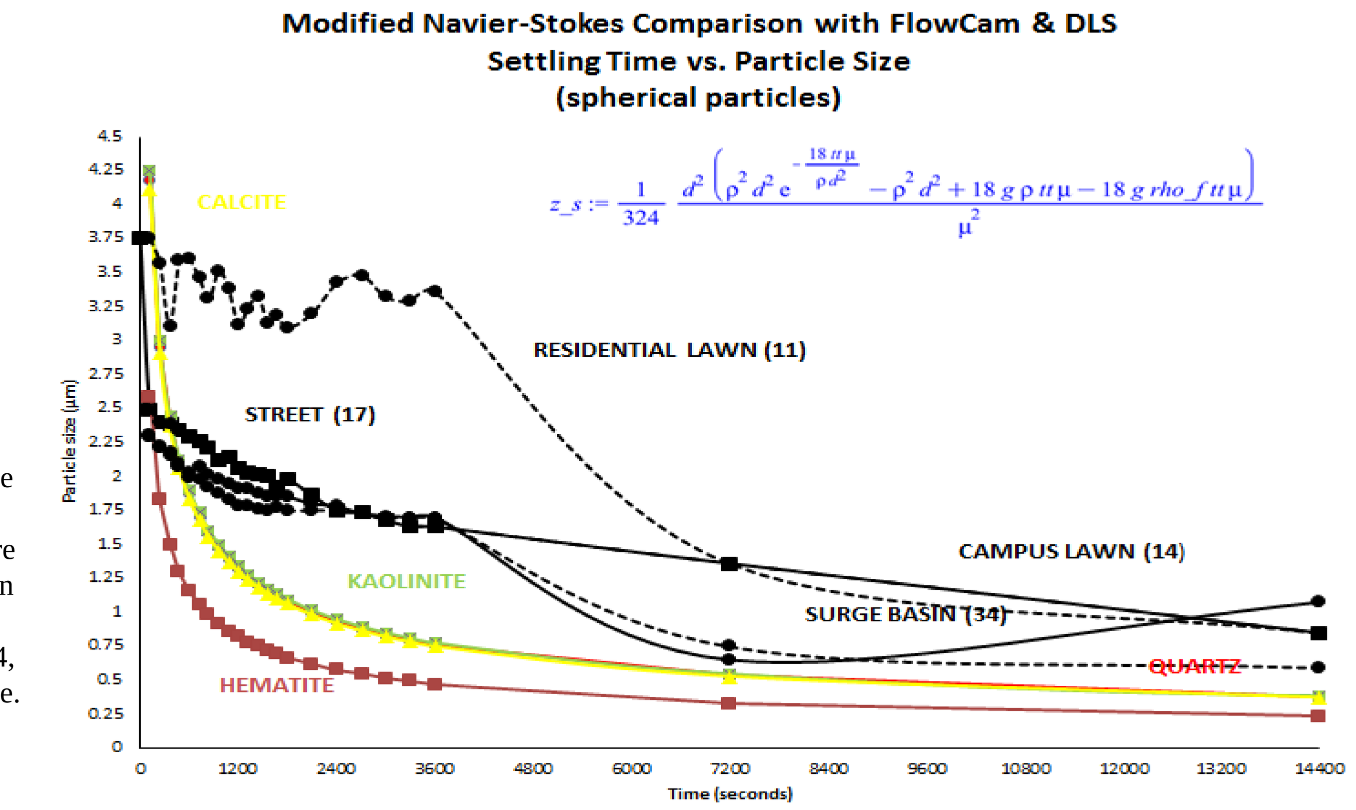


Figure 7. This graph shows the measured average particle size versus settling time from the FlowCam and DLS data (point to the white curves from each well) compared to a version of the Navier-Stokes equation with a term added to account for the non-spherical shape of the grains. Calcite, quartz, kaolinite, and hematite are shown here in comparison to the non-homogenous wells. Focus wells 11, 14, 17, and 34 are shown here.

Conclusions

This research aimed to quantify the size of suspended particles, correlate the composition of suspended particles to current land use, and distinguish anthropogenic or engineered nanoparticles from naturally occurring nanoparticles. Concentrations of suspended particles ranged from ~ 140- 4900 mg/L, with the mean particle diameters ranging from about 4 to 1 µm, and average particle aspect ratios of 0.74-0.81. Minimum circle fit values ranged from 0-0.43. Suspendable concentrations were highest under campus lawns, and lowest in the vicinity of residential lawns, a parking lot and former industrial site. Street and surge basin locations had intermediate levels of particles. The most angular particles occurred under lawns, and the least angular under streets and surge basins. Some particle shapes appeared to be engineered, though more work on shape analysis with statistics needs to be done. Graphite/graphitized carbon black and iron were detected in suspensions under streets and surge basins.

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