# Interaction of carbon nanotubes and graphene nanoplatelets with wastewater biomass

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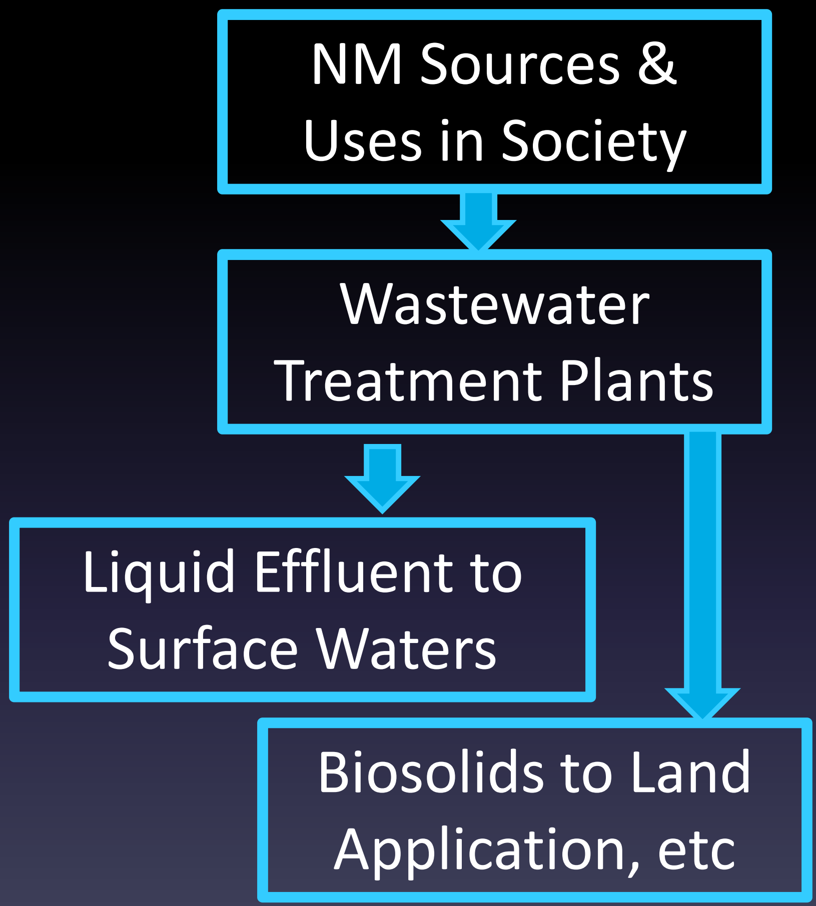
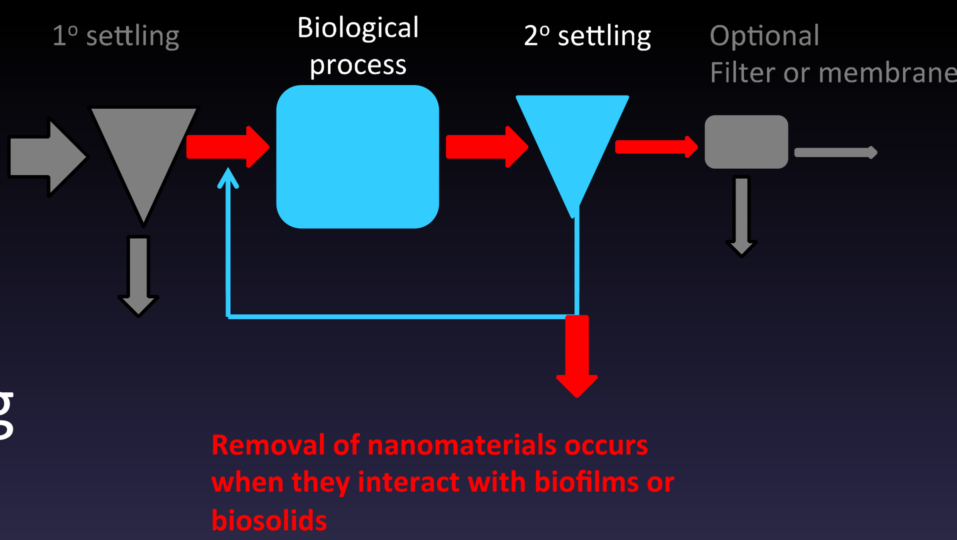
# Background


NM Sources & Uses in Society
Wastewater Treatment Plants
Liquid Effluent to Surface Waters
Biosolids to Land Application, etc

# Presentation Objectives

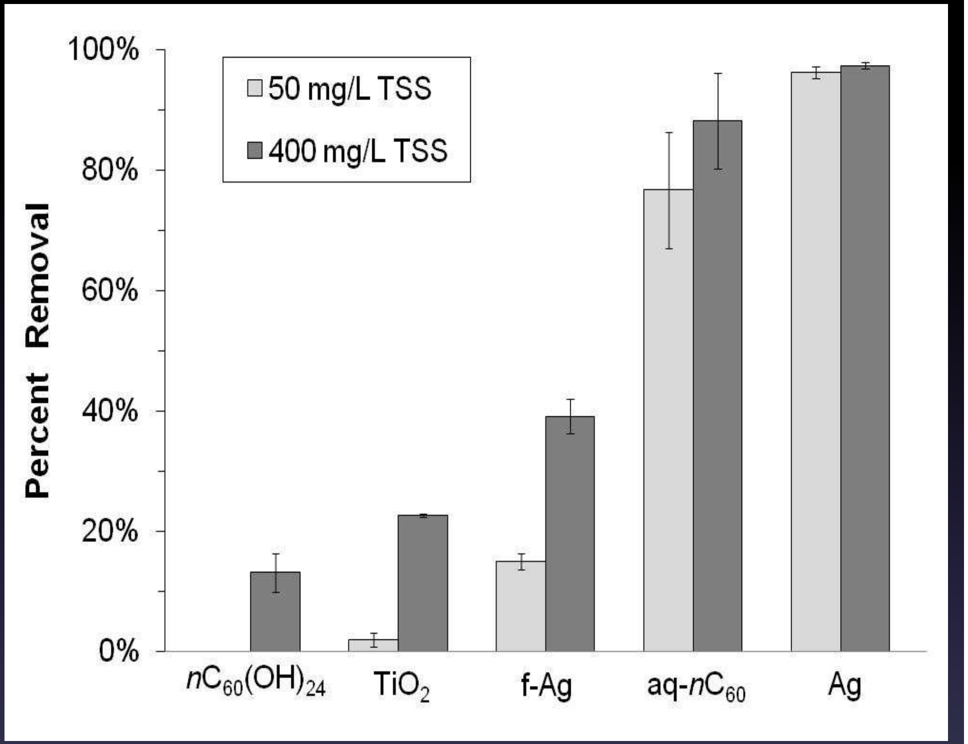
- Sorption of CNT & Graphene Oxide to wastewater biomass

- Overcoming analytical challenges in measuring graphene oxide in presence of biomass



# Carbon Nanomaterials

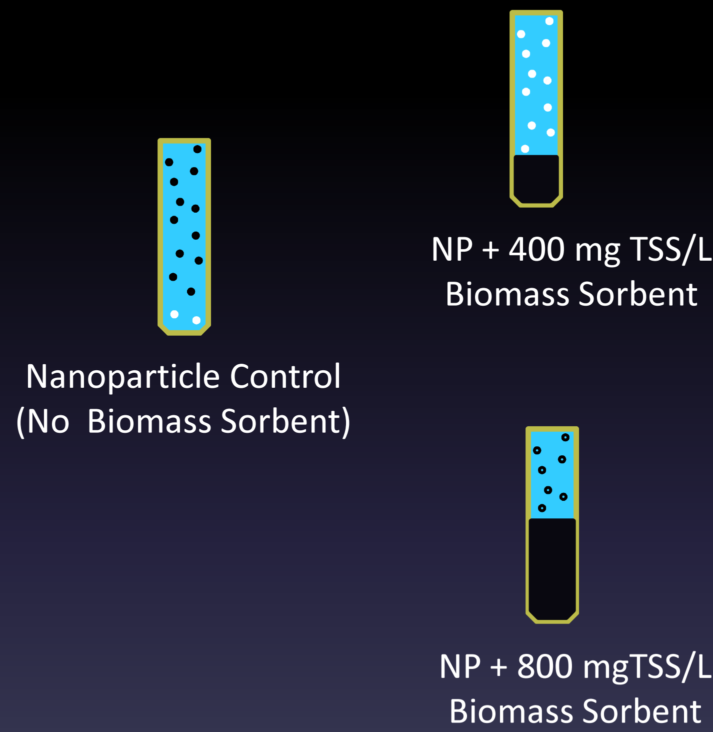
- 2-D materials
  - Graphene
  - Graphene Oxide
- 3-D materials
  - Fullerenes/fullerols
  - SWCNT
  - MWCNT
    - Functionalized
    - Non-functionalized
- Wide variety of applications
- Little information on interaction with wastewater biomass exists




*Kiser et al., Water Res., 2010*

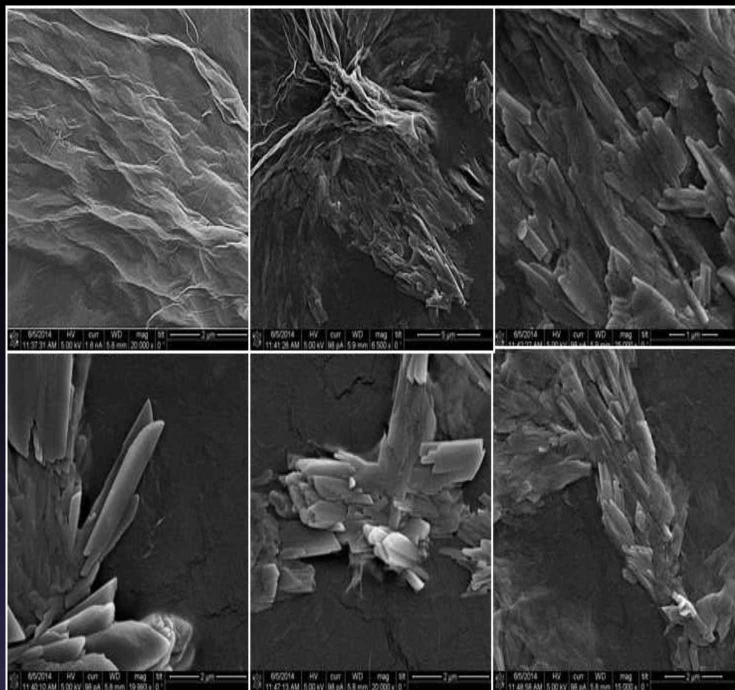
# Batch Sorption Experiments

- Prepare nanomaterials in 1 mM $NaHCO_3$
- Fresh wastewater biomass
- Mixing time = 3 hours
- Settling time = 30 min
- Centrifuge out biomass (if needed) = 5 min at 1000 G
- Analyze supernatant for nanomaterial
- Quick test



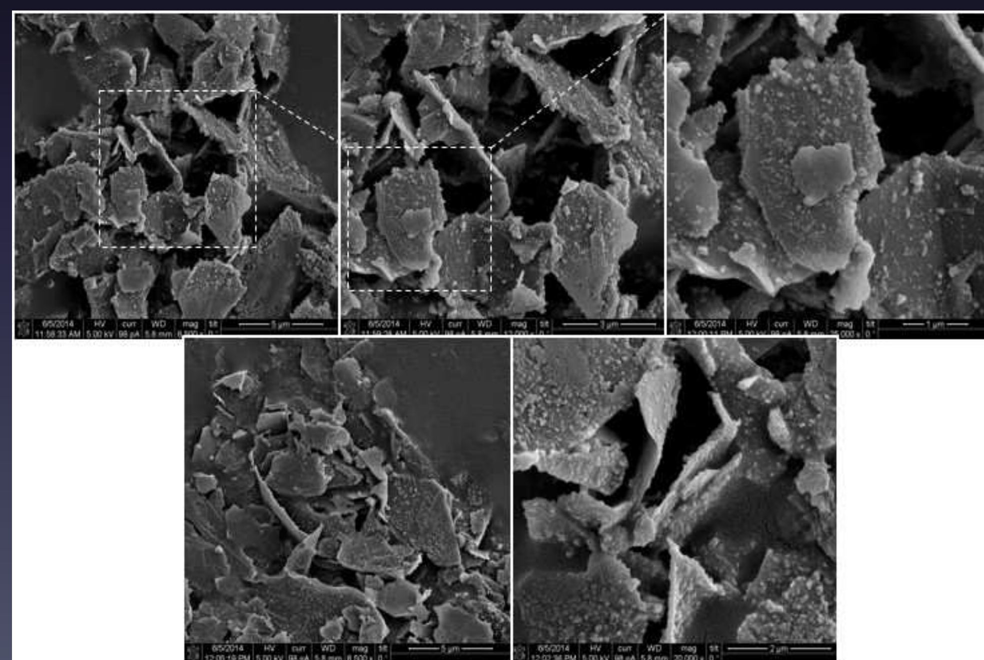

*Kiser et al., ES&T (2012)*

# GO & Few-Layer Graphene (FLG)



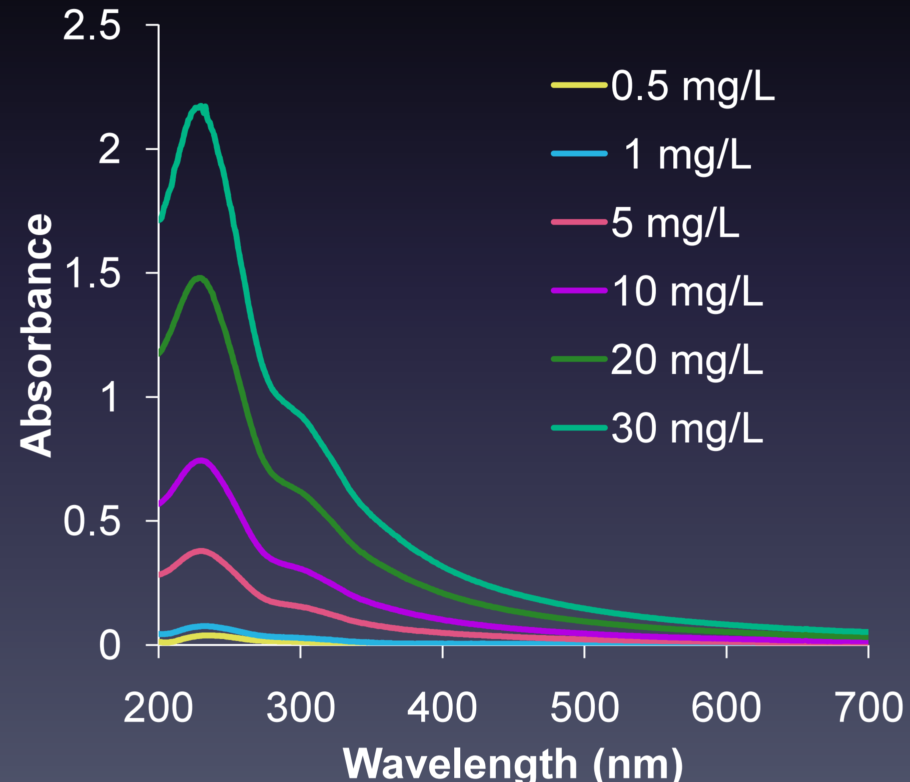
SEM images of GO

SEM images of FLG
(with gold sputtering)

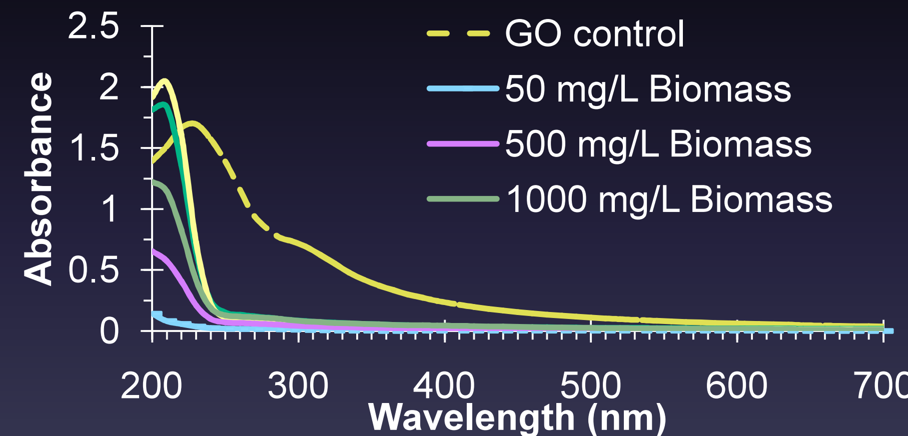


# Graphene Oxide (GO) Results

- GO analysis at high concentrations achievable by UV/VIS



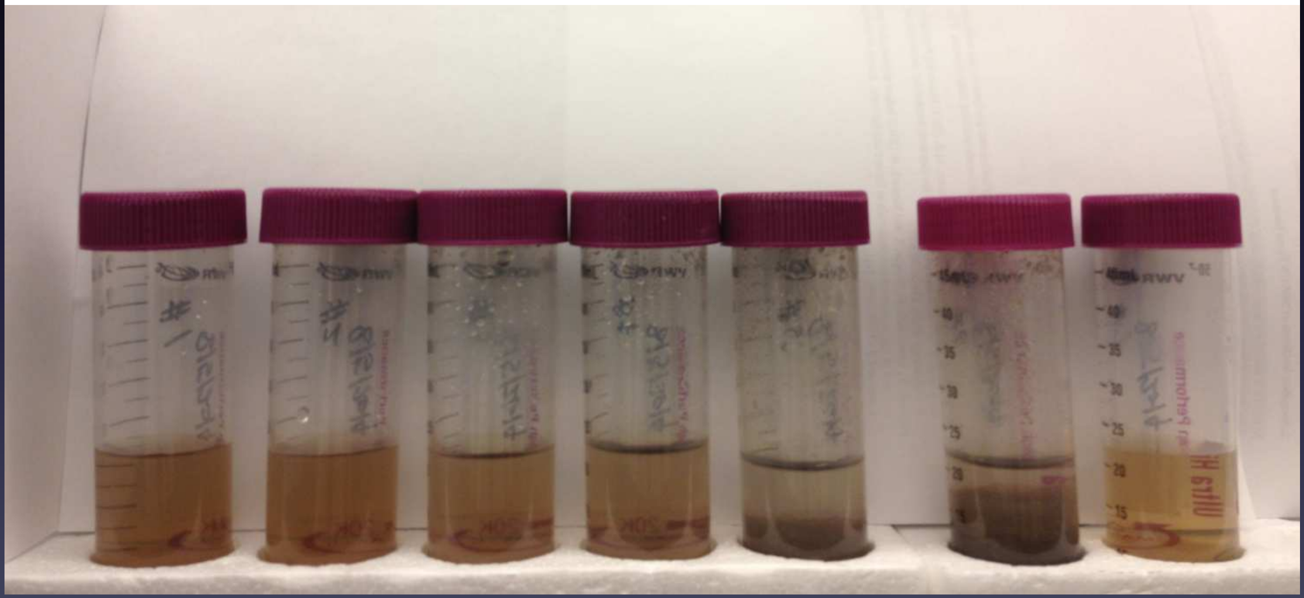

- Biomass can “release” soluble organics during 3 hr batch sorption that cause absorbance




- Approach- subtracted out background signals to quantify GO sorption

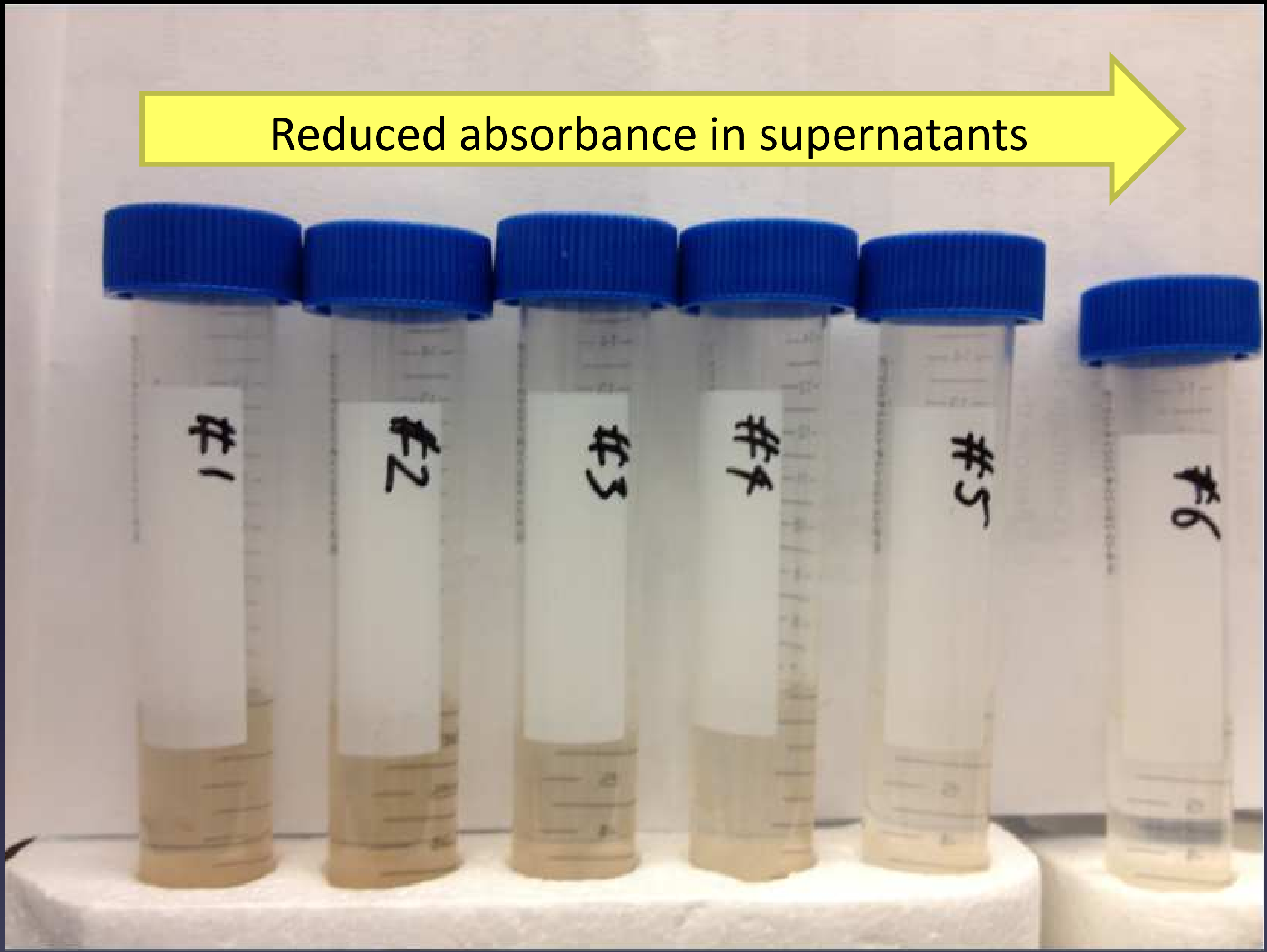
# Initial GO Concentration = 25 mg/L

After mixing for
3 hrs and settled for 30 min



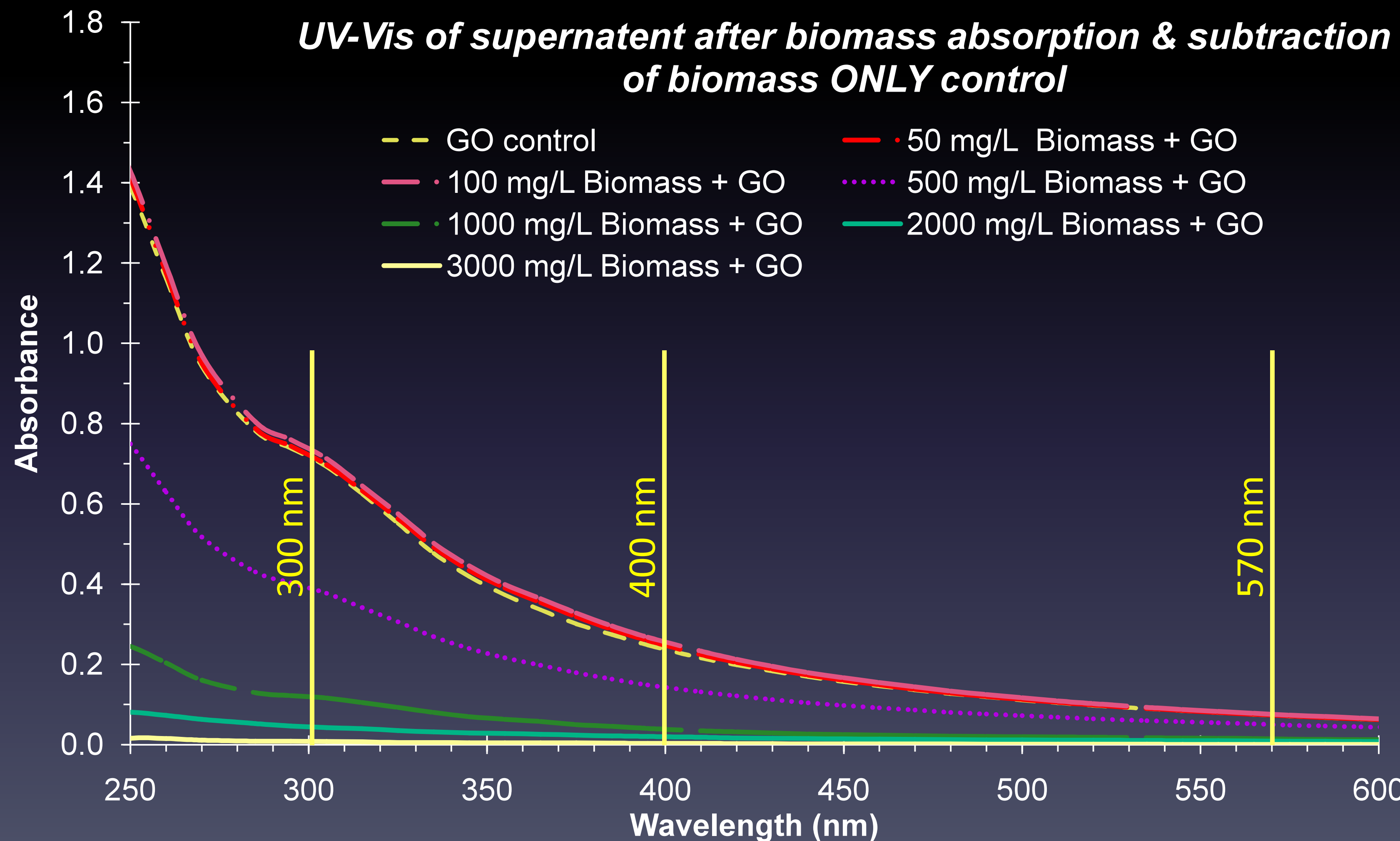
Biomass: 50 mg/L 100 mg/L 500 mg/L 1000 mg/L 2000 mg/L 3000 mg/L GO control

Supernatant after centrifuged at 1000 G for 5 min

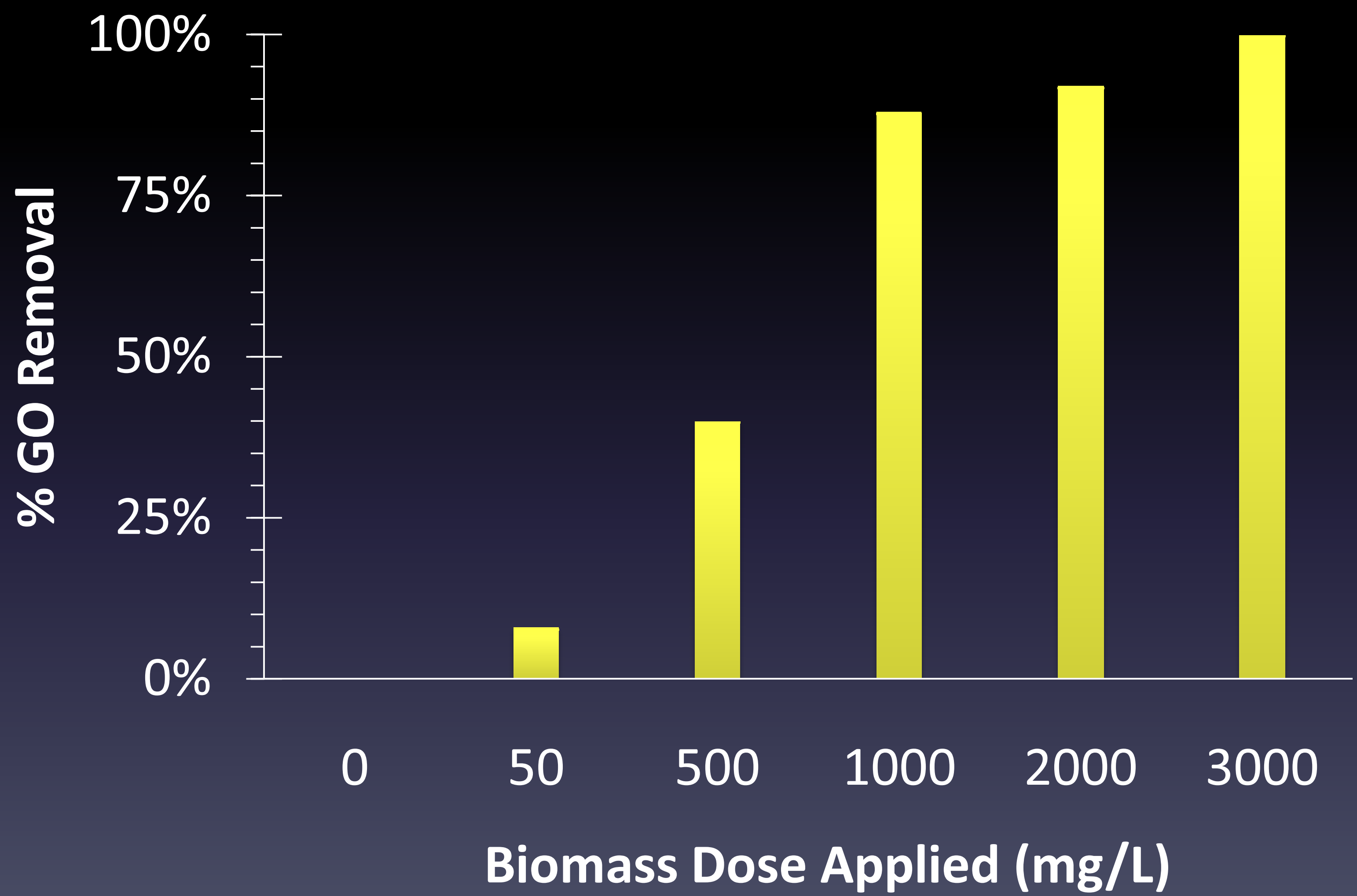



Biomass: 50 mg/L 100 mg/L 500 mg/L 1000 mg/L 2000 mg/L 3000 mg/L

# After subtracting the absorbance of biomass control



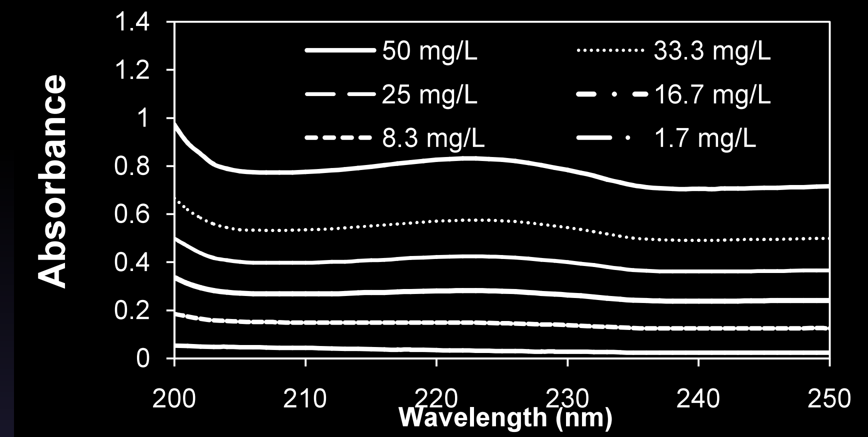
# GO Association with Biomass

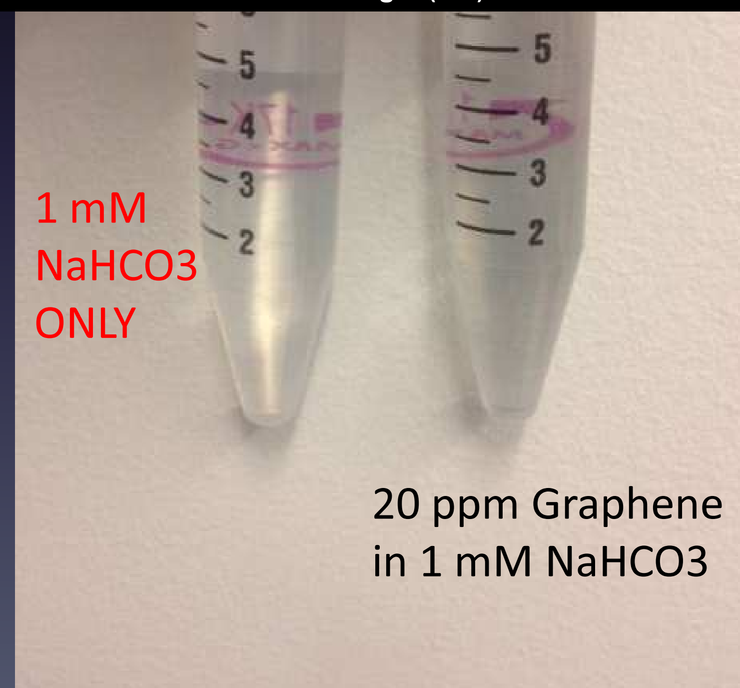


# Graphene - Biomass

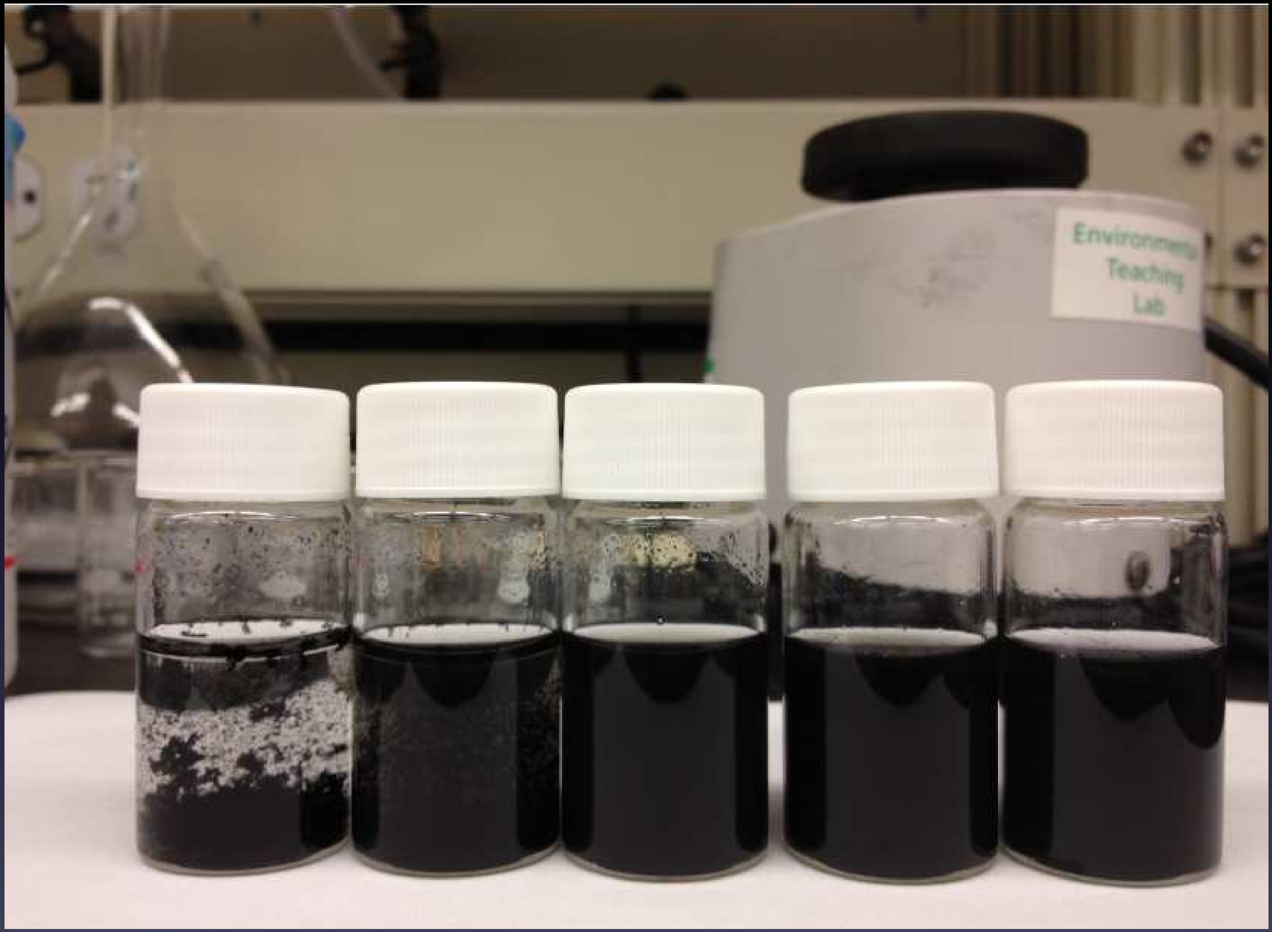
- Similar approach for graphene as GO
  - Lower absorbance from light scattering
- Graphene Removal with Biomass:
  - 0% removal with 50 mg/L biomass
  - 10% removal with 100 mg/L biomass

Flat Absorbance profile out to 700 nm



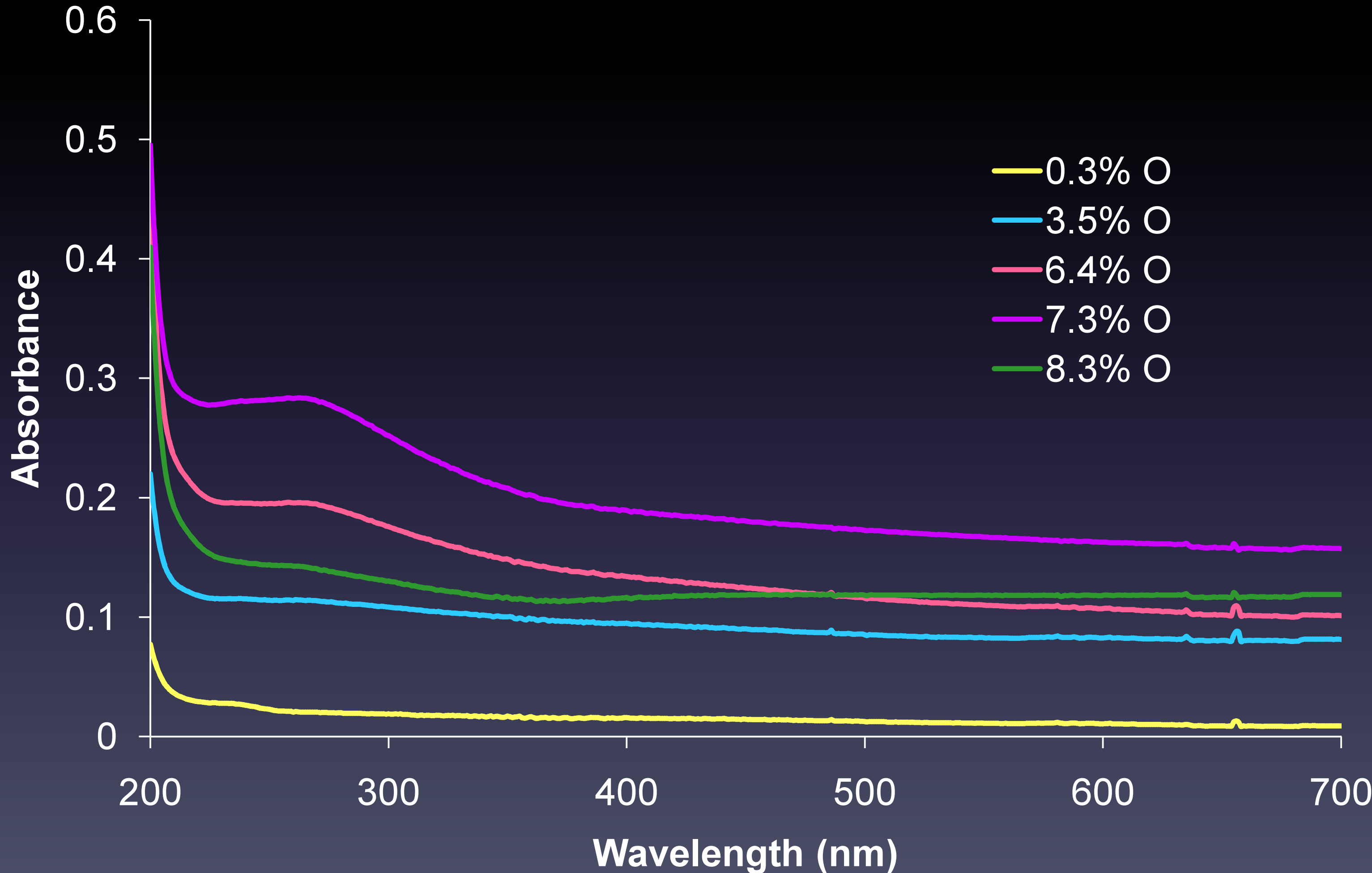
Functionalized CNT Samples (from H. Fairbrother/ JHU)
After Sonicate for 1 hr



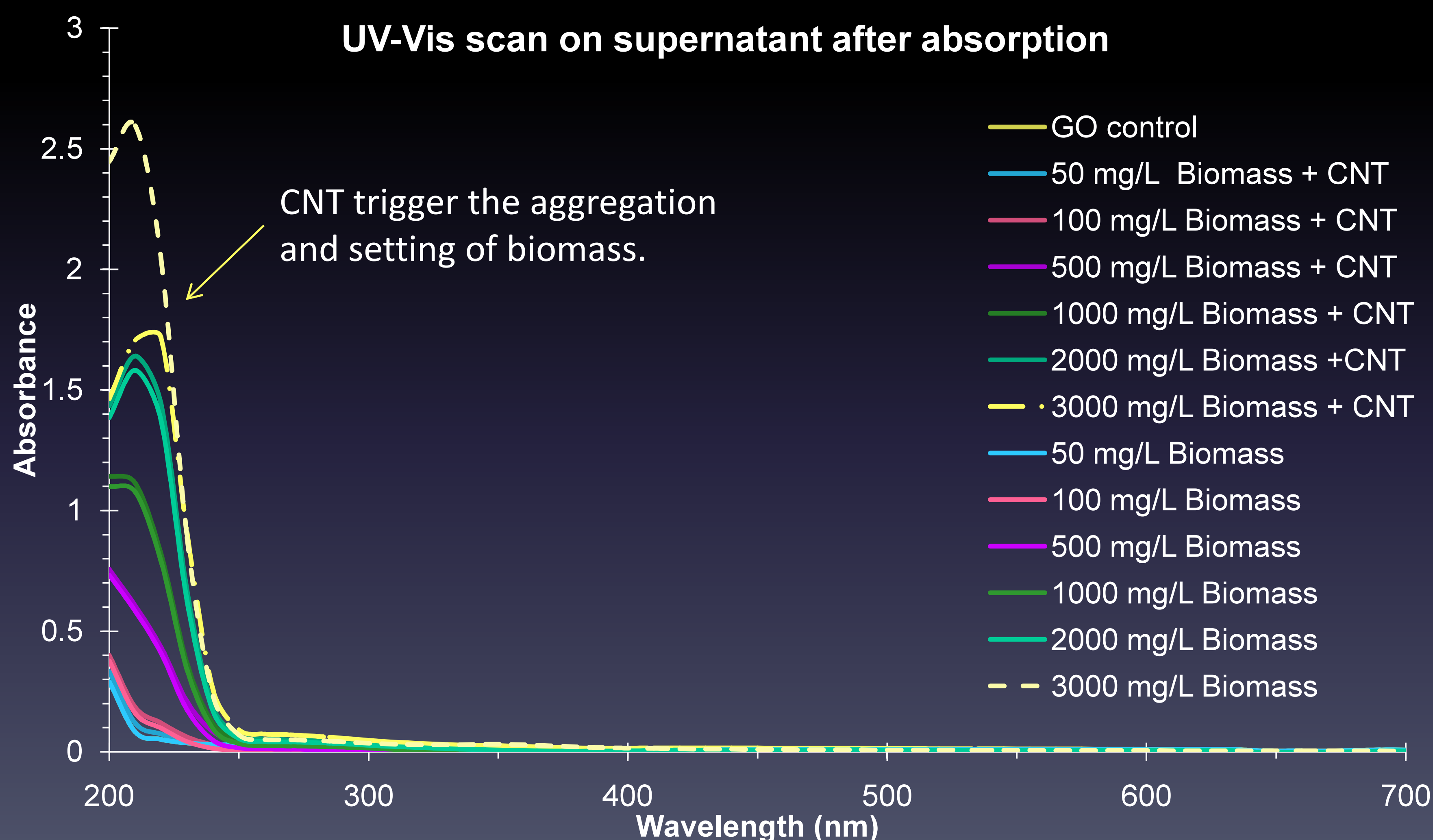

CNTs with different percentage of Oxygen:

0.3% 3.5% 6.4% 7.3% 8.3%

# UV-Vis Scan on 25 mg/L of CNT suspension



# Absorption of CNT with 8.3% O on the biomass



# Samples of CNTs with 8.3 % Oxygen

After mixing for 3 hrs and settled for 30 min

Even in Control sample (complete removal of CNTs)

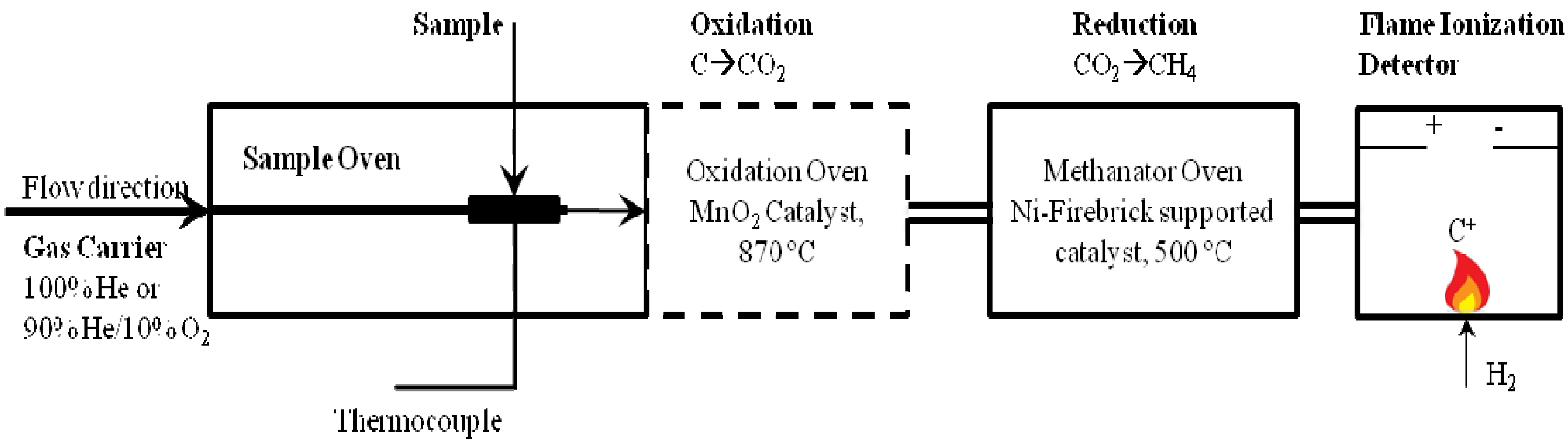
Biomass had no adverse effect on CNT removal

Biomass: 50 mg/L 100 mg/L 500 mg/L 1000 mg/L 2000 mg/L 3000 mg/L CNT Control

# Challenges

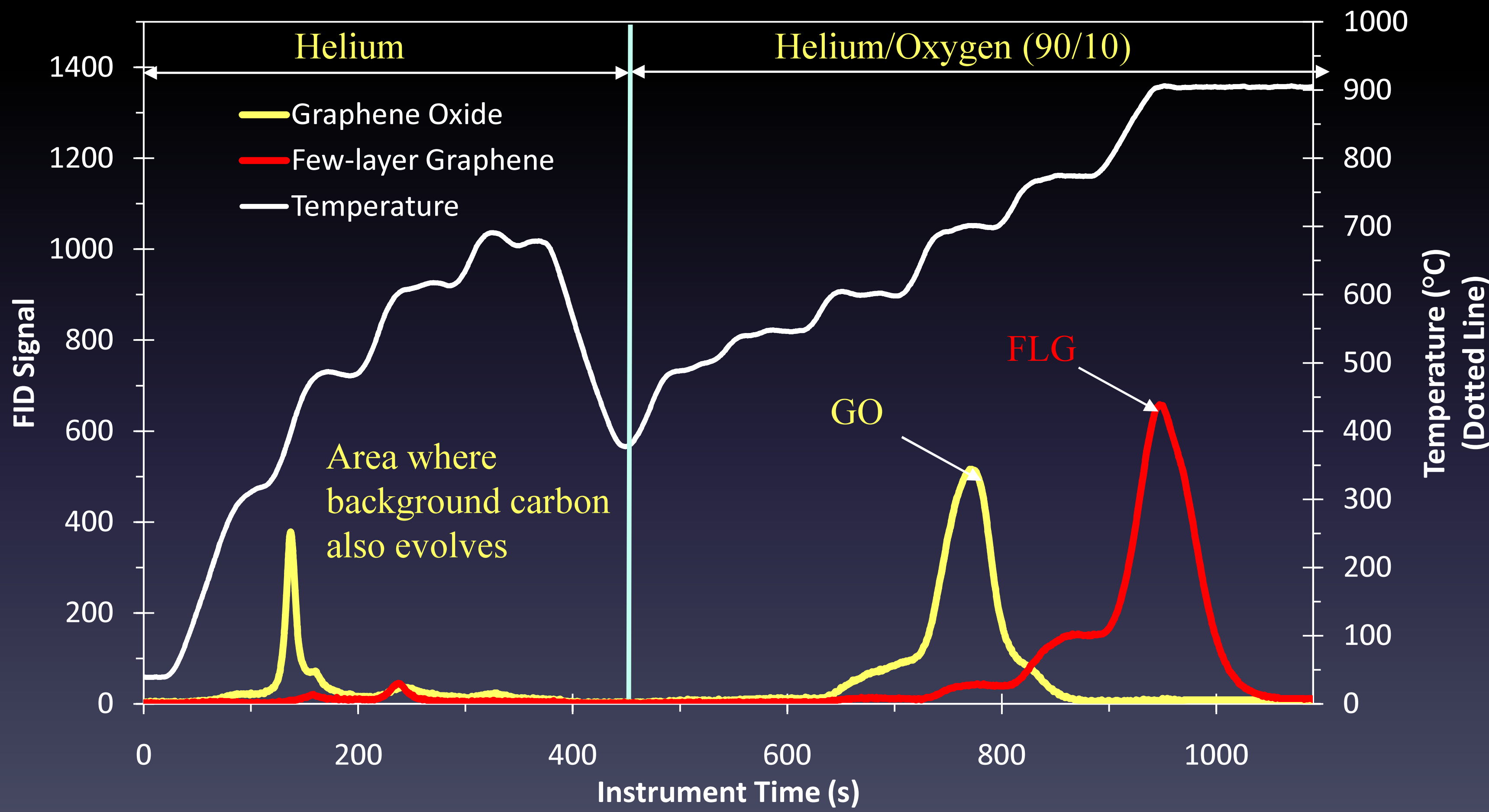
- Low level GO or CNT analysis not possible by UV/VIS alone
  - Biomass causes background UV/VIS interference
  - UV/VIS is non-specific
- Need a specific GO (CNT) analytical method
- Quantification using thermal combustion methods have worked well previously for CNTs
  - We previously observed challenges for oxidized CNTs because surface oxygen "burned" CNTs at similar temperatures as organic matter
  - Thermal methods have low detection limits for CNTs of ~ 3 ug (Doudrick et al., ES&T 2012)

# Elemental Carbon/Organic Carbon Analyzer

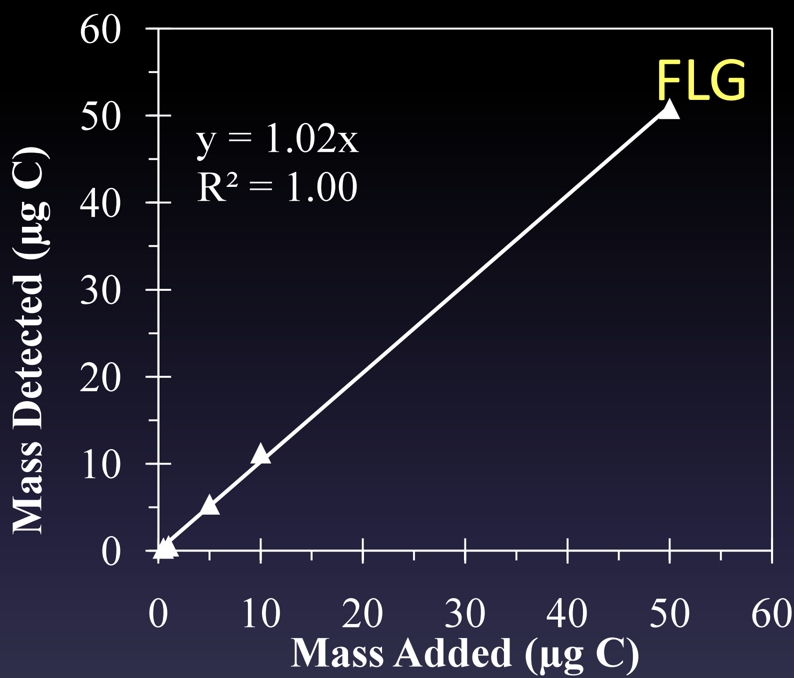


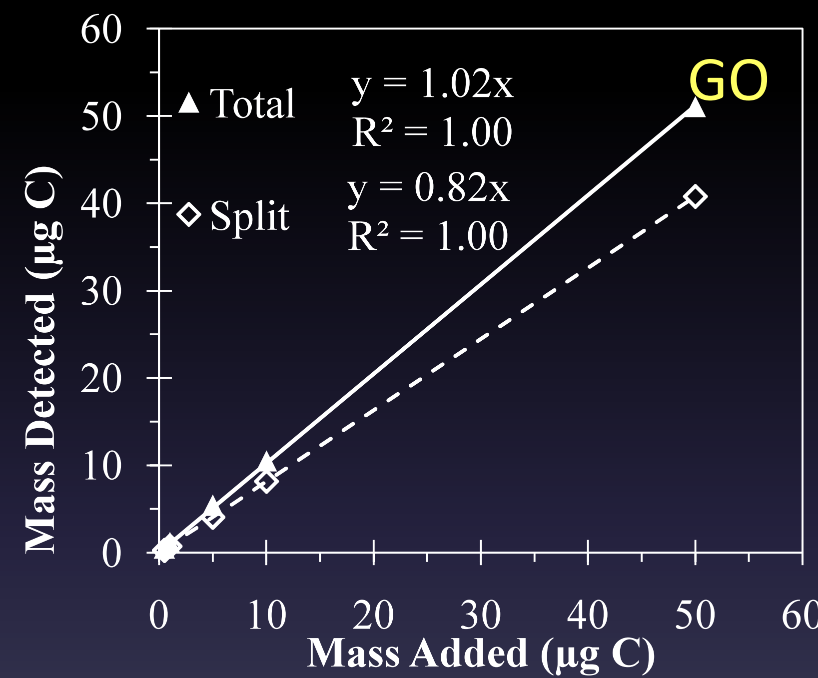

Sunset Laboratories Lab OC-EC Aerosol Analyzer

# Programmed Thermal Analysis (PTA)



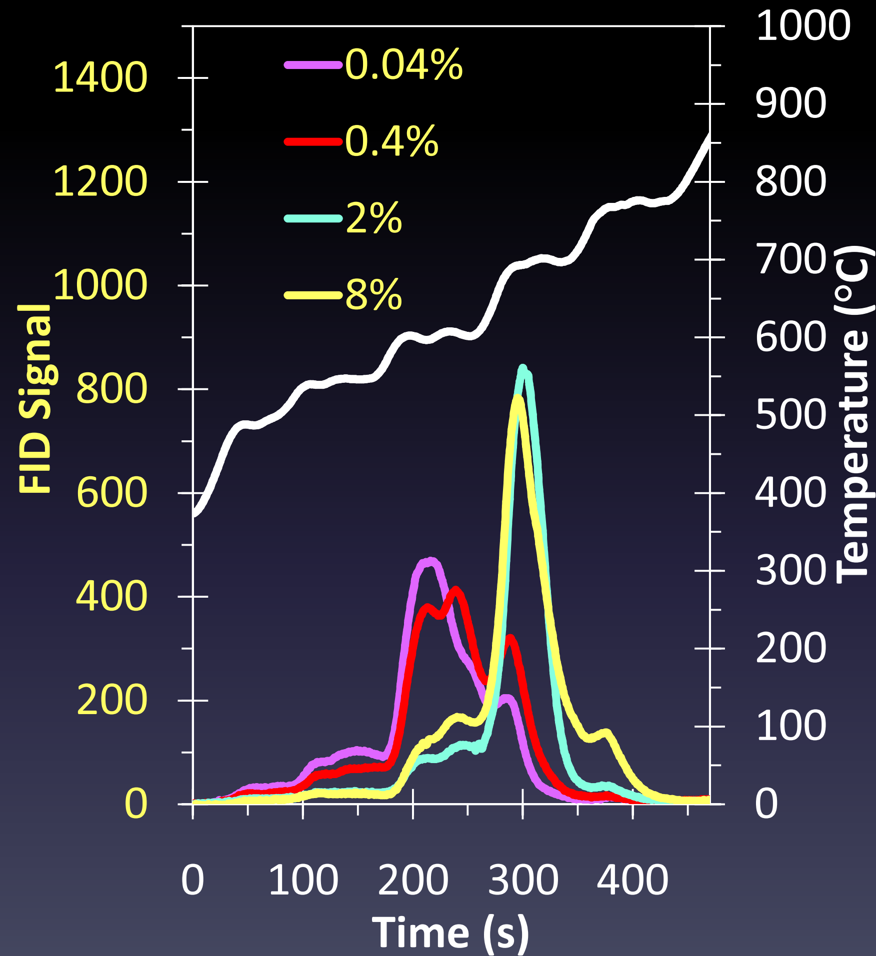
# Sensitive calibration curves



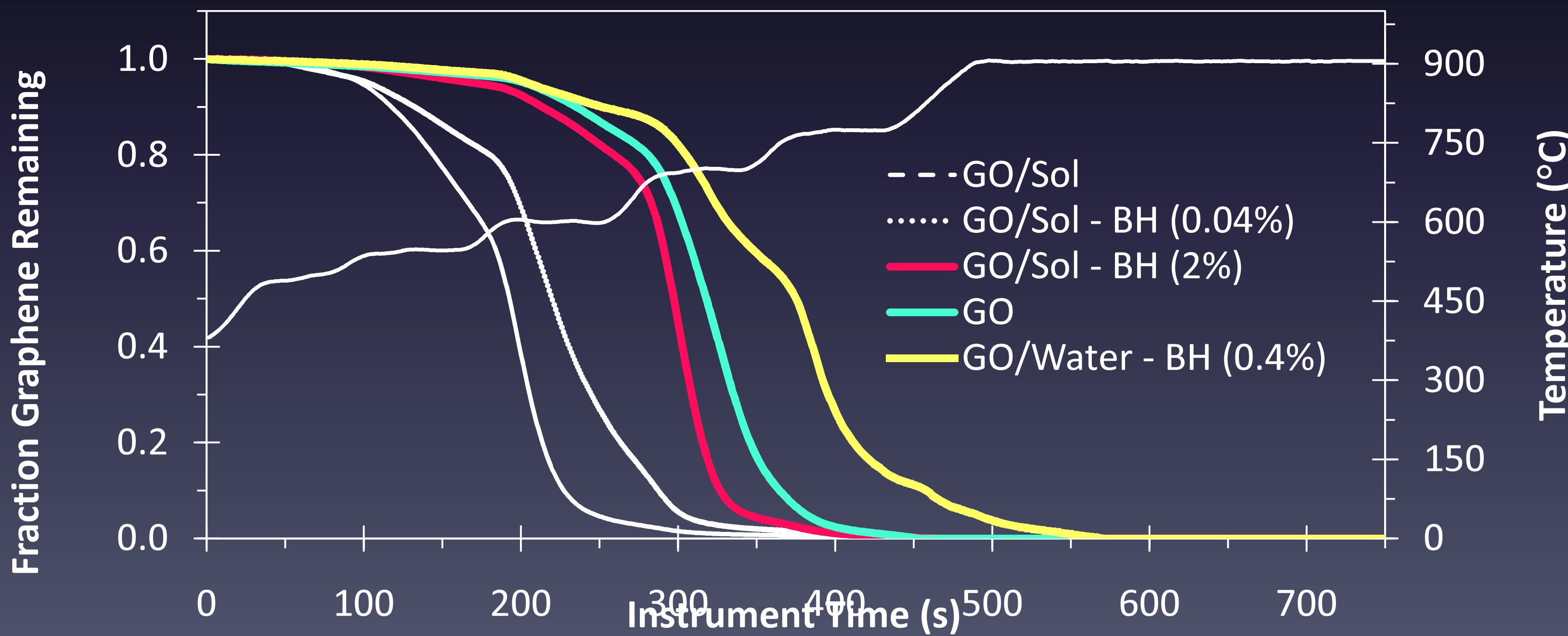
# Improve separation of GO signal from background organics

- Add reductant ($NaBH_4$)
- Reduced graphene oxide (RGO) analysis by XPS yields decreases number of C-O & C=O bonds by > 5 fold
- PTA thermogram improves

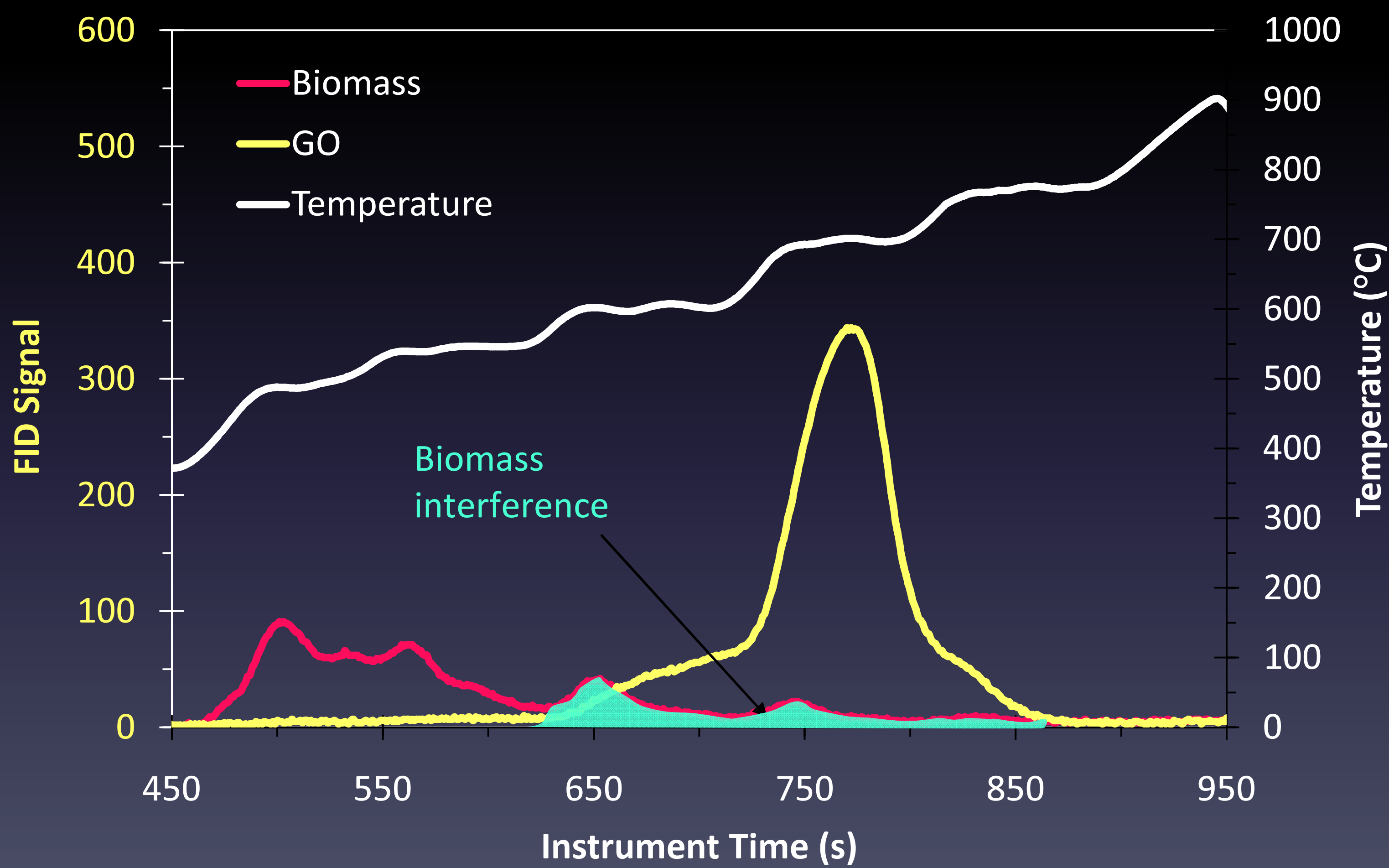


# Adding Solvable™ to degrade organics

- Solvable is an alkaline digestate that degrades organics; surfactant helps separation
- Solvable + $NaBH_4$ produces good pellet for separation & analysis

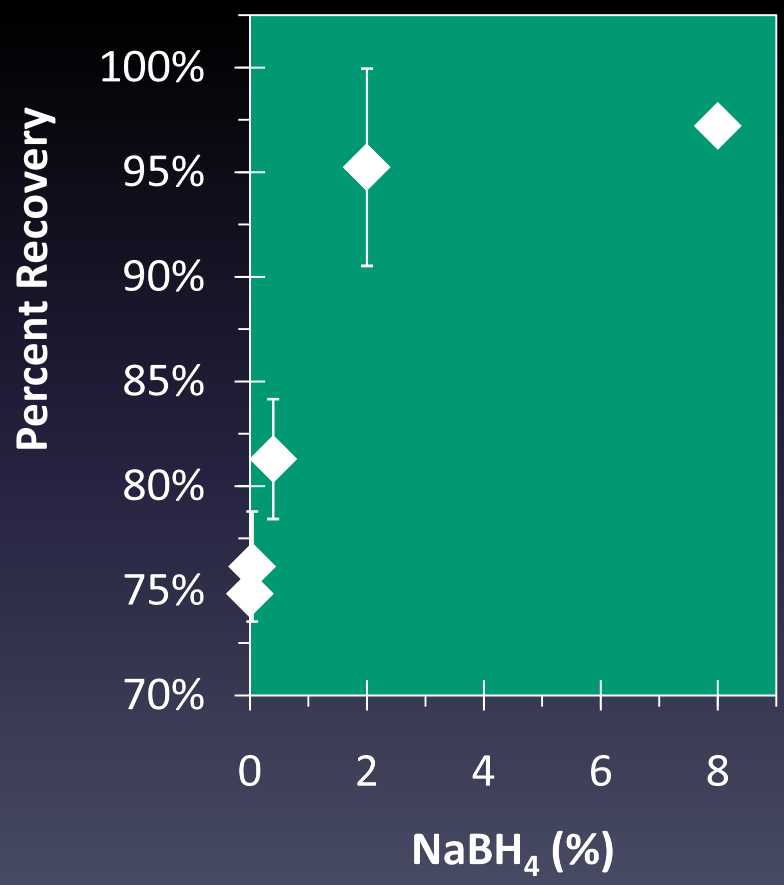


# PTA for GO & Wastewater Biomass (after Solvable + 2% $NaBH_4$)

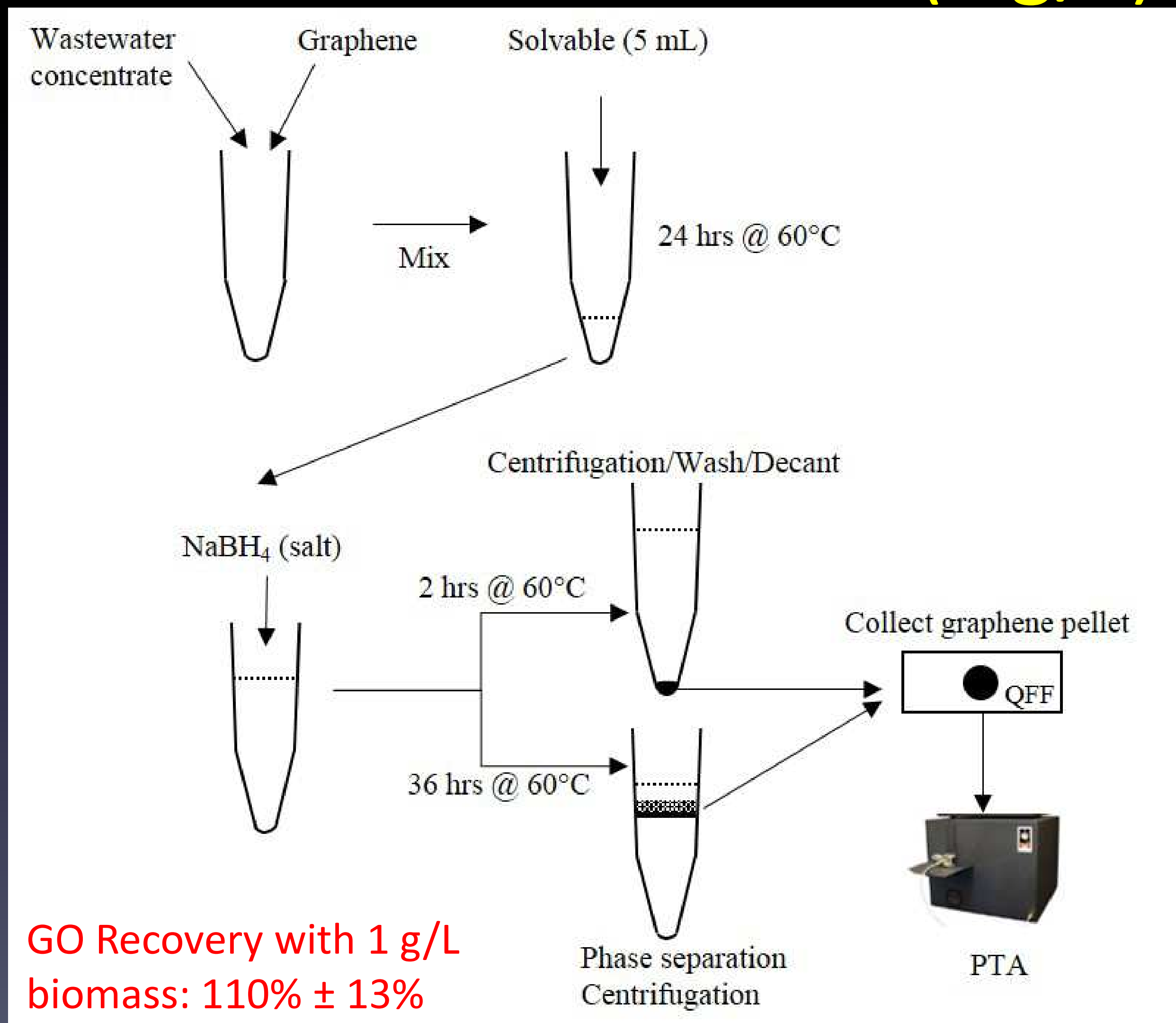


# GO or FLG spiked into wastewater biomass

- Allows quantification *in* biomass (rather than in water column as achieved by UV/VIS)
- Detection limits (MDL) are ~ 2 ug GO or FLG
- Higher recoveries: 80% to 110%
- Low background interference at low biomass doses*



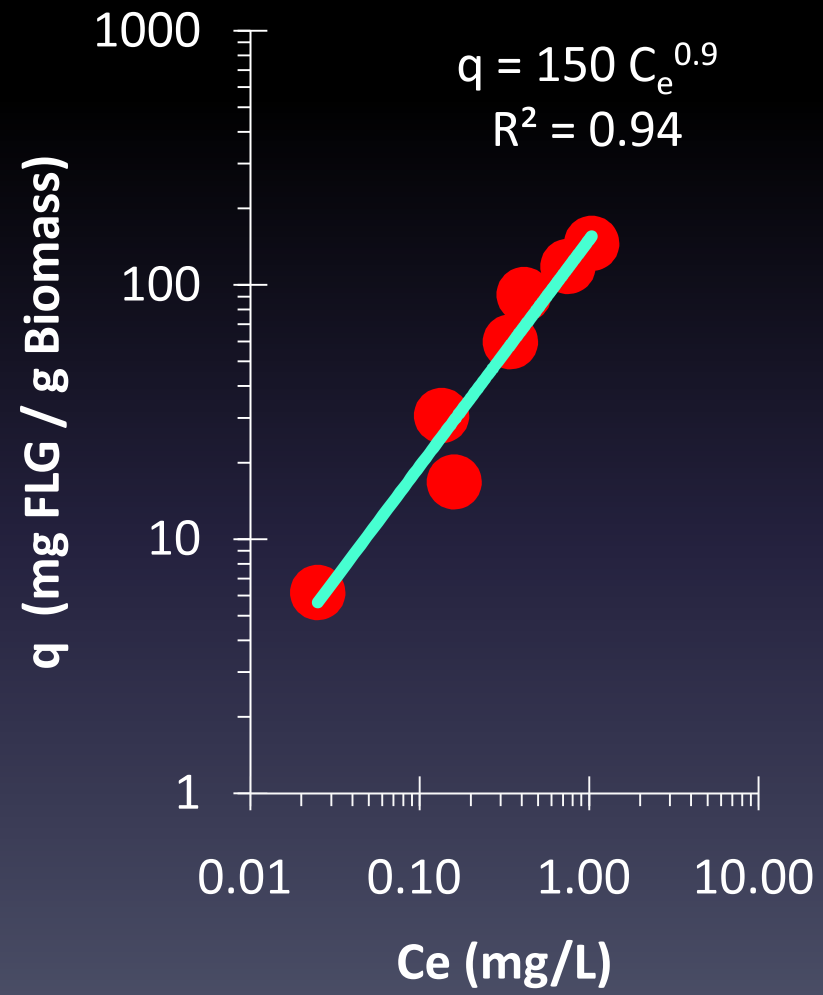
# Final Digestion Method to Handle Separation of FLG, GO (or CNT) from High Biomass Concentrations (1 g/L)




GO Recovery with 1 g/L biomass: 110% ± 13%

# Application to FLG sorption to Biomass

- Fixed biomass concentration
  - 50 mg/L
  - Higher biomass concentrations are now capable with optimized digestion method
- Variable initial graphene concentration
  - 0.3 to 8.3 mg/L
  - Lower than with UV/VIS
  - Very small background PTA signal from 50 mg/L biomass
- Consistent removal (10±3%) of graphene by 50 mg/L biomass



# Conclusions

- Functionalized CNTs
  - Dispersible in water
  - Readily aggregate, settle within pH and mixing conditions relevant to wastewater treatment (even without biomass)
- Graphene oxide & graphene:
  - Associates with biomass and will accumulate in biosolids
  - Existing analytics (UV-VIS) were limited to high concentrations
  - UV/VIS able to quantify GO or FLG in supernatant
- PTA was developed for GO & FLG in Biomass
  - Optimized method uses Solvable + 2% $NaBH_4$
  - Low detection limits
  - Allows determination of GO in biosolids

# Acknowledgements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