Size-Based Fractionation and Quantification of Mobile Colloids and Colloidal Organic Carbon in Field Samples

Jing Yan[1] (yanjing@udel.edu), Xia Meng[2] and Yan Jin[1]

[1]University of Delaware, Newark, Delaware, USA, [2]Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Kunming, Yunnan, China.

INTRODUCTION

- Natural colloids, *i.e.* entities with sizes from 1.0 nm to 1.0 µm, have large surface areas therefore high reactivity with and ability to facilitate the transport of contaminants in the subsurface environment;
- Quantification of smaller colloid fractions (< 0.45 µm), which are operationally considered as "dissolved" species in most studies, is lacking;
- The role of mobile colloids in carbon cycling, especially the carbon associated with < 0.45 µm fraction and/or colloidal organic carbon, in natural ecosystems has been largely overlooked.

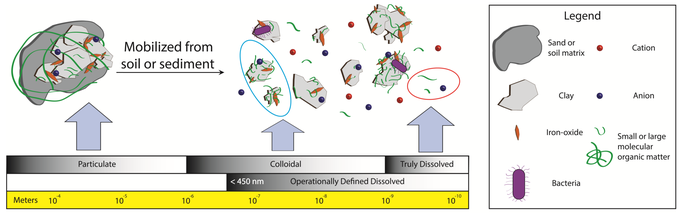
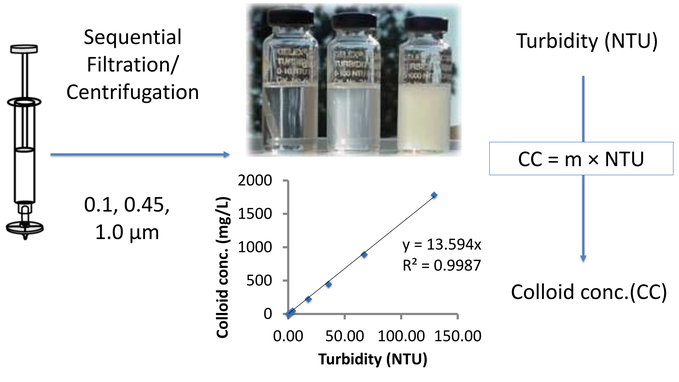


Figure 1. Schematic representation of colloid mobilization and colloids' association with organic carbon. Length scale corresponds to sizes of particulate, colloidal, truly dissolved and operationally defined dissolved phases.

OBJECTIVES

- To develop an experimentally and economically efficient methodology to quantify natural colloids in different size fractions (0.1-0.45 and 0.45-1.0 µm);
- To quantify possible underestimation of actual mobile colloid load due to the use of conventional size cutoff (< 0.45 µm) for separating "dissolved" phase;
- To quantify the amount of carbon associated with different size fractions of mineral colloids.

METHODOLOGY



- Turbidity-colloid concentration correlations were determined for soil colloids in two size fractions (0.1-0.45, 0.45-1.0 µm) based on measurements for 37 soils from the U. S. and Denmark;
- Using the correlations, colloid concentrations were determined for samples collected from agricultural, forestry, wetland and estuary ecosystems at various sampling times;
- Total organic carbon (TOC) in different size fractions (e.g. < 10 kDa, 0.1, 0.45, 1.0 µm) were quantified.

RESULTS

Effects of colloid size on turbidity-colloid curves

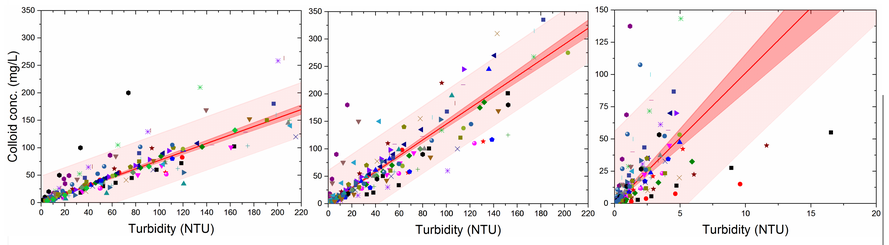


Figure 2. Scatter plots and regression curves of the turbidity and mass concentration of soil colloids from 37 soils in different size fractions: 0.45-1.0, 0.10-0.45 and < 0.10 µm (from left to right).

- Most data fall on the same turbidity-concentration curve with acceptable variation, except for < 0.1 µm colloids;
- Slopes of turbidity-concentration curves increase with decreasing colloid size.

Effect of colloid composition on turbidity-colloid relations

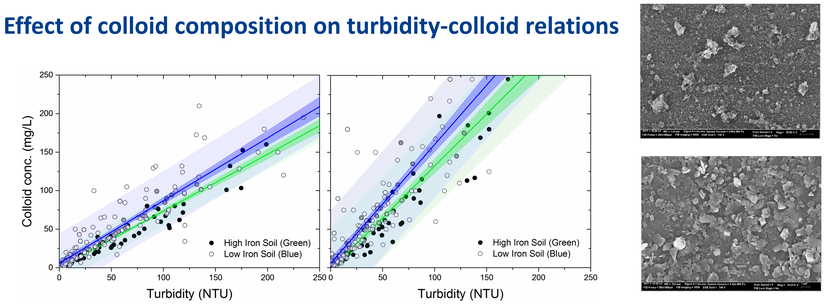


Figure 3. The scatter plots and regression curves of the turbidity and the mass concentration of colloids from low and high iron soils; the SEM images of colloids (0.45-1.0 µm) in high and low iron soils (top to bottom)

- Slope of turbidity-concentration curve increases with increasing free iron oxides content;
- Iron oxides have different light scattering properties from clay minerals.

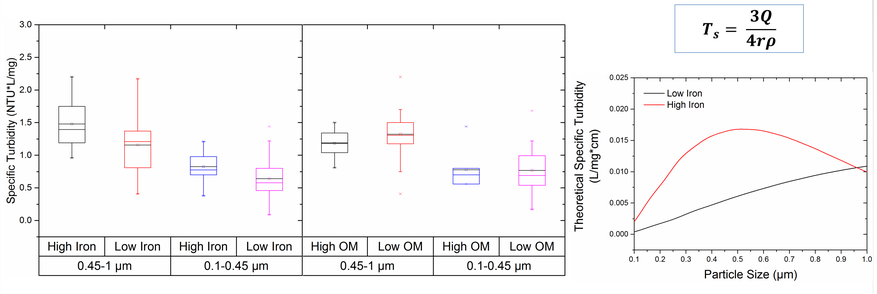


Figure 4. Specific turbidity of colloids in soils with different iron and organic carbon content; theoretical equation and plots of specific turbidity based on Mie theory (r: colloid radius; ρ: colloid density; Q: scattering coefficient)

- The specific turbidity (T_s) indicates the light scattering intensity per unit mass of colloids;
- High free iron oxides (> 0.5% Fe oxide) → Large T_s;
- No significant difference in T_s for different organic carbon content (1.0 - 30.9% OC);
- T_s shifts are theoretically proved by Mie theory.

RESULTS

Colloid and TOC concentrations in field samples

- 66.0±22.7% of natural colloids (0.10-1.0 µm) were smaller colloids (0.10-0.45 µm);
- Up to 94% of organic carbon was observed in the smaller size fraction;
- Positive correlation between colloid concentration and TOC content was observed.

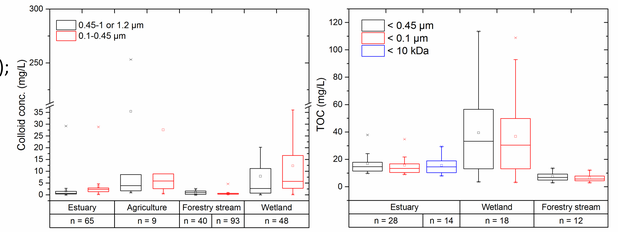


Figure 5. Colloid and TOC conc. in different size fractions in various natural ecosystems.

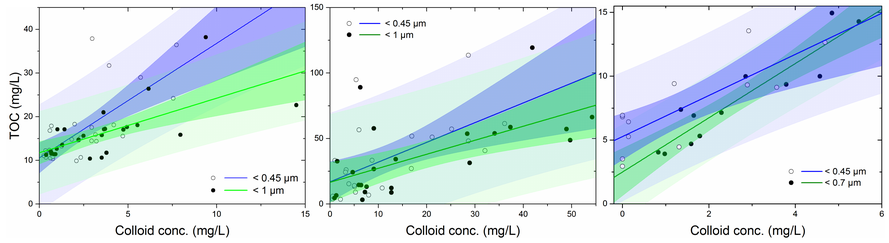
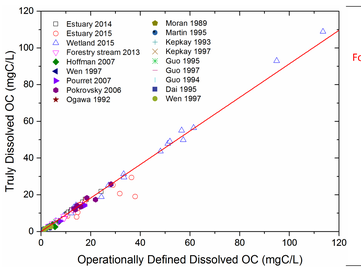


Figure 6. Correlation between colloids and TOC in estuary, wetland and forestry stream sample sites (left to right)

Ratio of colloidal organic carbon in "dissolved" organic carbon



Sample ID	Sample Site Description	Lower/Upper cutoff size	DOC_{tr}/DOC_{od}
Estuary 2014	Chesapeake Bay, MD	0.10/0.45 µm	0.93
Estuary 2015	Chesapeake Bay, MD	10 kDa/0.45 µm	0.74
Wetland 2015	Wetlands, DE	0.10/0.45 µm	0.94
Forestry stream 2013	Streams, MD	0.10/0.45 µm	0.87
Hoffman 2007	Rivers, WI and MI	10 kDa/0.40 µm	0.70
Wen 1997	Rivers, TX	10 kDa/0.45 µm	0.68
Pourret 2007	Ground water, Central Brittany, France	10 kDa/0.20 µm	0.81
Pokrovsky 2006	Rivers, central Siberia, Russia	10 kDa/0.22 µm	0.90
Ogawa 1992	Pacific ocean, Honshu, Japan	10 kDa/0.45 µm	0.96
Moran 1989	Sea water, Nova Scotia, Canada	10 kDa/0.45 µm	0.85
Martin 1995	Venice Lagoon, Italy	10 kDa/0.40 µm	0.84
Kepkay 1993	Bedford Basin, Nova Scotia, Canada	10 kDa/0.20 µm	0.75
Kepkay 1997	Bedford Basin, Nova Scotia, Canada	10 kDa/0.20 µm	0.94
Guo 1995	Gulf of Maxico and Mid Atlantic Bay	10 kDa/0.20 µm	0.90
Guo 1997	Chesapeake Bay and Galveston Bay	10 kDa/0.20 µm	0.92
Guo 1994	Gulf of Maxico	10 kDa/0.40 µm	0.88
Dai 1995	Rhone Delta, Switzerland	10 kDa/0.40 µm	0.81
Wen 1997	Gulf of Maxico	10 kDa/0.45 µm	0.72

Figure 7. Correlation between Truly Dissolved and Operationally Defined Dissolved OC (DOC_{tr}, DOC_{od}) from this study (hollow points in figure, red in table) and previous works (solid points in figure, black in table)

- DOC_{tr}/DOC_{od} ratios ranged from 0.68-0.94 and the regression ratio was ~0.92, indicating colloidal organic carbon can contribute at least 8% and up to 32% OC to DOC_{od}.

SUMMARY

- Size-dependent turbidity-concentration correlations were obtained for 0.45-1.0 and 0.10-0.45 µm colloids and they can be used for quick quantification of colloid concentration in field samples;
- More than half (66.0±22.7%) of natural colloids (0.10-1.0 µm) were < 0.45 µm, indicating that the operationally defined size cutoff underestimates the colloidal pool in all aqueous samples tested;
- At least 8% of organic carbon in the DOC_{od} is colloidal; this may have important implications in assessing the fate of organic carbon hence in regional or global carbon budget estimations.

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