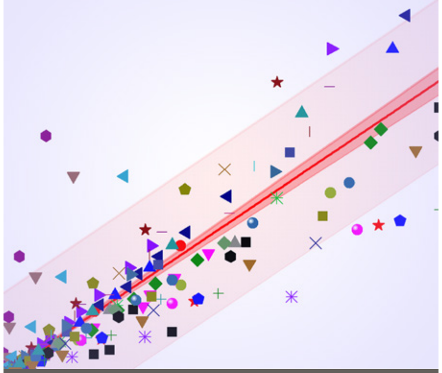
Technical Notes



Core Ideas

- An efficient turbidimetric method was developed to quantify colloids in aqueous samples.
- Concentration–turbidity correlations depend primarily on particle size rather than composition.
- The size-dependent correlations have practical and nearly universal applicability.
- This method allows accurate and quick colloid quantification in field samples.

Size-Dependent Turbidimetric Quantification of Suspended Soil Colloids

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Mobile soil colloids play an important role in affecting soil hydraulic properties and soil formation, as well as in facilitating the transport of strongly sorbing constituents (e.g., contaminants, pesticides, nutrients) in subsurface environments. Accurate quantification of mobile colloids is thus essential for understanding and prediction of soil element migration, changes in soil hydraulic properties, and colloid-associated contaminants in natural and managed systems. However, quantification of colloids in field samples, especially the <0.45-μm fractions, which are traditionally considered dissolved solutes, has largely been hindered due to the lack of reliable methods. In this study, we developed a simple and efficient methodology of using size-dependent correlations between nephelometric turbidity and mass concentrations of colloids for quantifying colloids in the <0.1-, 0.1- to 0.45-, and 0.45- to 1.0-μm fractions. The correlations were measured using model colloids (latex, silica, and Fe oxide particles) and soil colloids extracted from 37 soils. We found that colloid size strongly affected concentration–turbidity relationships, while colloid composition played a less important role in shifting the correlations. The size-dependent concentration–turbidity correlations were further tested against gravimetric measurements using additional field samples and found to be more accurate than correlations that do not consider size effects. The relatively insignificant particle composition effect indicates the practically "universal" applicability of the reported correlations. In addition, the correlations, for the first time, allow quantification of colloids in different size fractions in environmental samples. This would enhance our capability to more accurately quantify the colloidal pools in natural systems, which have strong implications for understanding the processes and mechanisms of colloid and colloid-associated-constituent mobilization and transport.

Abbreviations: CML, carboxylate modified latex; NTU, nephelometric turbidity units; OM, organic matter; UV-Vis, ultraviolet-visible.

Soil colloids (~1 nm–1 μm in size) (Everett, 1972; Lead and Wilkinson, 2007) are complex mixtures of organic and inorganic entities with supramolecular structure and properties (Baalousha et al., 2011; Kretzschmar et al., 1999; Vold and Vold, 1983). Because of their small size and large surface area, hence high reactivity and the ability to facilitate the transport of contaminants in the subsurface environments, mobilization and transport of colloids have attracted much research attention (Baalousha et al., 2011; de Jonge et al., 2004a; Flury and Qiu, 2008; Kretzschmar et al., 1999; Lead and Wilkinson, 2007). While many studies have identified and analyzed the behavior of soil colloids in aquatic samples, quantitative information on the environmental occurrence of the colloids, especially those in the size fraction of <0.45 μm, is scarce. The main reasons for this scarcity are: (i) <0.45-μm colloids are considered "dissolved" by the operational practice of filtration in most studies and therefore not quantified (Doucet et al., 2007; Lead and Wilkinson, 2007); and (ii) an economically feasible and technically effective method that can determine colloid concentration in field samples is absent (Filella, 2007). The operational definition of colloids (i.e., >0.45 μm) together with the lack of reliable quantification methods could greatly underestimate the colloidal pools in natural systems. As a result, concentrations of chemical and biological constituents (e.g., C, nutrients,

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organic contaminants and heavy metals, and microbial pathogens, etc.) in the “dissolved” pool would be overestimated because they would include the constituents that are sorbed onto the <0.45-μm colloidal particles. This overestimation and the inability to distinguish accurately the “state” (sorbed vs. dissolved) of these constituents hinder our ability to determine their environmental fate. Therefore, it is essential to quantify the small colloidal fractions (<0.45 μm) and to examine the role of these fractions in the fate and transport of colloid-associated constituents.

Quantification of colloid concentration has been accomplished by a variety of methods, including gravimetric determination (Degueldre et al., 1990; Vilks et al., 1991; Yan et al., 2016), light scattering (Filella et al., 1997), ultraviolet-visible (UV-Vis) or fluorescent spectrophotometry (Haiss et al., 2007; Koynov and Butt, 2012; Wang et al., 2015a), scanning electron or transmission electron microscopy (Domingos et al., 2009; Mavrocordatos et al., 2007), and laser-induced breakdown detection (Kim and Walther, 2007; Walther et al., 2006). Among these methods, gravimetric, UV-Vis and fluorescent spectrophotometry, and light scattering methods are more frequently used due to their relative simplicity and lower cost. However, the use of the gravimetric method is greatly limited by its requirement for large volumes of samples, while colloid concentrations in environmental samples are in general low. While the sample volume requirement is less a limiting issue for the UV-Vis and fluorescent methods, these analyses are greatly interfered with by light-absorbing dissolved substances and thus are not suitable for samples with a colored background, e.g., samples containing humic substances (Gippel, 1995). In contrast, light scattering techniques, especially nephelometric turbidimetry, have the advantages of higher sensitivity, wider detection range, less interference, and smaller sample-volume requirement and therefore have been widely used in studies of sediment and colloid transport (de Jonge et al., 2004b; Jacobsen et al., 1997; Minella et al., 2008; Pfannkuche and Schmidt, 2003; Rügner et al., 2013; Schelde et al., 2002).

Success of the nephelometric turbidimetry method depends on reliable correlations between turbidity and particle concentration. While various linear correlations between turbidity and particle concentration have been used for the quantification of total suspended solids or suspended particulate matter in freshwater lakes and rivers (Minella et al., 2008; Pfannkuche and Schmidt, 2003; Rügner et al., 2013), these correlations were developed based on and for measurements of larger particles (2–100 μm). Only a few studies have attempted quantification of smaller particles (<2 μm) such as soil colloids (de Jonge et al., 2004b; Jacobsen et al., 1997; Schelde et al., 2002) and industrial nanoparticles (Greswell et al., 2010). Furthermore, these correlations are generally regarded as particle- or field site-specific and therefore have been applied as such. To date, no “universal” correlations, to the best of our knowledge, exist. Indeed, the effects of particle size and composition, especially size, on turbidity–sediment concentration correlations have been reported in previous studies (Foster et al., 1992; Gippel, 1995). However, detailed and systematic evaluation and quantification of the effects of particle size and composition on turbidity measurements, especially for <1.0-μm soil colloids, have not been performed to date.

The objective of this study was to develop size-dependent turbidimetric correlations to quantify soil colloids in different size fractions in environmental samples. For this purpose, concentration–turbidity correlations were first measured for model colloids (latex, silica, and Fe-oxide particles) to examine the effects of colloid size and composition, respectively, on the correlations. Similarly, concentration–turbidity correlations were then developed for soil colloids prepared from a large number of soil samples (37 soils collected from the United States and Denmark). These samples were fractionated into different size fractions (<0.1, 0.1–0.45, and 0.45–1.0 μm) and measures for size-dependent correlations between mass concentrations of dispersed soil colloids and turbidity. These correlations were further validated by comparing the estimated concentration values from turbidity measurements using the correlations against gravimetric measurements of additional environmental samples.

Materials and Methods

Model Colloids

Carboxylate modified latex (CML, Molecular Probes, Thermo Fisher Scientific), silica (Nissan Chemical America Corporation), goethite, and hematite were used as model colloids (e.g., uniform size and pure composition) to investigate the effects of particle size and composition on concentration–turbidity correlations. The CML and silica colloids are spherical particles, while hematite and goethite colloids are ellipsoidal and needle-shaped. Purchased CML with diameters of 0.04, 0.1, 0.35, 0.42, 0.6, and 1.2 μm and silica particles of 0.2 μm were directly dispersed in deionized water by sonication for 5 min. Goethite (length: 1–2 μm, width: 0.09 μm) and hematite (0.25 μm) particles were synthesized following the method of Schwertmann and Cornell (2000) and then dispersed to obtain colloid suspensions. More details on the synthesis method and particle characteristics were provided in previous studies (Wang et al., 2015b, 2015c). Mass concentrations of goethite and hematite suspensions were determined gravimetrically, while the concentrations of CML and silica suspensions were calculated based on the original stock concentrations and dilution factors. Suspension turbidity was determined using a nephelometer (HACH) and reported in nephelometric turbidity units (NTU).

Soil Samples

We collected or obtained from colleagues a total of 37 soil samples, 15 from the United States and 22 from Denmark. The soils, which represent different elemental compositions (e.g., organic C, Fe content) and soil texture, were air dried and passed through

2-mm sieves prior to use. Characteristic properties of these soils, including soil texture and relevant chemical composition, are summarized in Table 1. Soil texture was determined based on particle size analyses using the hydrometer method (Bouyoucos, 1962) and laser diffraction method (Eshel et al., 2004). Soil organic C (SOC) content was determined with a LECO analyzer coupled with an infrared CO_2 detector (Thermo Fisher Scientific) or converted from soil organic matter (SOM) content (i.e., the loss-on-ignition method [Nelson and Sommers, 1996]) using the Van Bemmelen factor of 0.58 (i.e., SOC = 58% SOM [Van Bemmelen, 1890]). The content of total “free” Fe oxides, which affects the light scattering properties of particles (Ishida et al., 1991; Lafon et al., 2006), was determined by the dithionite–citrate–bicarbonate extraction method (Loeppert and Inskeep, 1996).

Colloid Fractionation and Quantification

Air-dried soil samples were gently crushed and passed through a 0.05-mm sieve. Prior to particle size fractionation, all soil samples were dispersed in deionized water at a soil/water ratio of 1:10, shaken for 24 h, and sonicated for 15 min to disintegrate aggregates and obtain water-dispersible soil colloids. The dispersed colloids were fractionated into three size fractions (<0.1, 0.1–0.45, and 0.45–1.0 μm) by sequential centrifugation, which is briefly described as follows. First, bulk soil suspensions were centrifuged at 221 × *g* for 8 min to settle out particles >1.0 μm, and then colloids <1.0 μm in the supernatant were siphoned out into 50-mL centrifuge tubes. The supernatant with colloids <1.0 μm was further centrifuged at 884 × *g* for 10 min to settle out the 0.45- to 1.0-μm fraction. Finally, colloids <0.1 and 0.1 to 0.45 μm were separated from the <0.45-μm suspension from the previous step at 22,095 × *g* for 8 min. These selected centrifugation speed and time combinations were determined based on the study of Gimbert et al. (2005). To avoid alteration of the scattering characteristics of colloids by drying, fresh colloids settled by centrifugation were immediately resuspended with deionized water and used as stock suspensions. The mass concentration of colloids in the stock suspension was determined by weighing the dry mass of the settled colloids after drying 10- to 40-mL aliquots from the suspension at 105°C. From those measurements, concentration–turbidity calibration curves were generated for each size fraction.

Field Sampling, Preparations, and Measurement

To evaluate the applicability of size-dependent concentration–turbidity calibrations, soil pore water samples were collected from a field site at Blackbird State Forestry in New Castle County, Delaware (39°20′ N, 75°40′ W). To minimize sampling artifacts, a peristatic pump (Geotech) was used at a low flow rate of 100 mL/min (Ryan and Gschwend, 1990) to extract water from wells located at different soil depths. Samples were first fractionated into <0.1-, 0.1- to 0.45-, and 0.45- to 1.0-μm size fractions by centrifugation at the prescribed centrifuge forces and times as given above. Colloid concentrations in each size fractions were determined by the size-dependent concentration–turbidity correlations by measuring the turbidity (detailed method procedure is provided in the supplemental material) as well as directly measured gravimetrically (i.e., by weighing oven-dry samples on glass slides at 105°C with a microbalance) and compared.

Table 1. Characteristic properties of soils

Soil	Soil texture	Sand	Silt	Clay	Organic C	Free Fe oxides
		%				
CZO-R†	sandy clay loam	51.0	23.0	26.0	1.16	0.99
BV-R†	sandy loam	76.0	12.0	12.0	0.7	3.08
BV-G†	sandy clay loam	66.0	8.0	26.0	0.35	0.16
CM-Ag†	silt loam	29.0	51.0	20.0	2.21	0.64
CM-Pa†	loam	43.0	43.0	14.0	3.55	1.06
CM-Fo†	loam	50.0	38.0	12.0	2.97	0.52
Conrad†	fine sand	90.0	8.0	2.0	2.38	0.49
Potts†	NA‡	NA	NA	NA	0.70	0.49
Palouse†	silt loam	13.2	68.6	18.2	1.22	0.52
Walla Walla†	silt loam	8.3	78.4	13.3	1.05	0.34
Royal†	silt loam	30.7	63.1	6.2	0.47	0.31
Salkum†	silty clay loam	11.9	59.7	28.4	2.97	1.02
Red Bluff†	clay	17.9	36.5	45.6	1.40	2.09
Øbakker no. 101	NA	NA	NA.	NA	1.44	0.37
Øbakker no. 107	NA	NA	NA	NA	21.2	0.41
Øbakker no. 115	NA	NA	NA	NA	30.9	1.18
Øbakker no. 117	NA	NA	NA	NA	10.6	0.22
Norwegian FF	sandy loam	56.1	33.4	10.5	5.49	0.49
Greenland no. 1	loamy fine sand	84.2	12.5	3.3	2.04	0.26
Greenland no. 3	sandy loam	66.1	29.1	4.8	7.01	0.38
Greenland no. 24	loamy fine sand	77.3	18.2	4.6	2.24	0.31
Greenland no. 28	sandy loam	54.9	37.4	7.7	5.31	0.38
Greenland no. 39	loam	43.1	49.5	7.4	2.57	0.32
Greenland no. 47	sandy loam	65.9	30.8	3.4	4.95	0.23
Jyndevad no. 6	fine sand	90.3	4.9	4.8	1.69	0.57
Jyndevad no. 7	fine sand	90.8	4.5	4.7	1.61	0.56
Jyndevad no. 11	fine sand	90.4	4.9	4.6	1.93	0.59
Jyndevad no. 67	fine sand	90.8	5.0	4.2	1.97	0.36
Jyndevad no. 73	fine sand	90.8	5.0	4.2	1.99	0.35
Jyndevad no. 78	fine sand	90.8	5.0	4.3	2.11	0.35
Estrup no. 5	loamy fine sand	79.6	14.7	5.7	2.07	0.15
Estrup no. 6	sandy loam	75.7	17.6	6.8	2.07	0.17
Estrup no. 17	sandy loam	68.3	23.8	7.9	4.47	0.15
Estrup no. 53	sandy loam	62.1	28.6	9.3	5.69	0.16
Tylstrup no. 13	sandy loam	73.4	22.2	4.4	N.A.	0.20
AZ13†	sandy loam	58.1	15.4	10.5	1.60	0.89
AZ18†	sandy clay loam	51.4	21.6	27.0	2.31	2.33

† Soils from the United States; all others are from Denmark.
‡ NA, not analyzed.

Statistical Analysis

Linear regressions between turbidity and colloid mass concentration and 95% confidence and prediction intervals were obtained using the Origin software program (Origin Lab). To examine the size and composition effects on the concentration–turbidity correlations, Pearson's correlation coefficients were calculated between scattering properties of colloids, i.e., specific turbidity, and the content of soil clay, free Fe oxides, and organic C. Changes in the specific turbidity of colloids with changing colloid size were also analyzed using a one-way analysis of variance (ANOVA) combined with the Tukey–Kramer honest significant difference (HSD) to test the significance of differences in specific turbidity among different size fractions. Both Pearson's correlation and one-way ANOVA analyses were performed using JMP Pro 12.1.0 (SAS Institute). Additionally, linear regression analysis between gravimetrically measured and predicted colloid concentrations from the correlations was performed, and absolute and relative errors were used to evaluate the performance of correlations in predicting the colloid concentration.

Results and Discussion

Concentration–Turbidity Correlations of Model Colloids

Measured concentration and turbidity values for the suspensions of all model colloids, including CML of various sizes, silica, and Fe oxyhydroxides, are presented in Fig. 1. Strong correlations between colloid concentration and turbidity were observed for all colloids. Figure 1 clearly shows that, for the same type of colloid (e.g., CML), concentration–turbidity correlations strongly depend on particle size, as reflected by the increase in the slopes of those curves from ∼0.1 to ∼6.3 as the particle size decreased from 1.2 to 0.04 μm. The dependence is much more pronounced for smaller particles with sizes <0.1 μm or 100 nm, which is the cutoff size used to define nanoparticles (Baalousha et al., 2011), indicating that nanoparticles have very different light scattering properties than their larger counterparts.

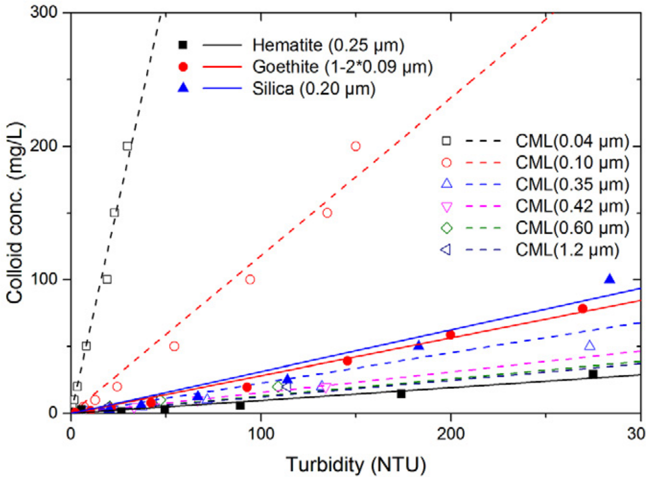

Fig. 1. Correlations between suspension turbidity and the mass concentration of model colloids (carboxylate modified latex, CML) with different sizes and compositions.

The effect of particle composition can also be observed in Fig. 1 by comparing the slopes of the concentration–turbidity curves of 0.09-μm goethite and 0.1-μm CML with those of 0.25-μm hematite, 0.35-μm CML, and 0.2-μm silica colloids at the same concentrations. The goethite curve has a much smaller slope than the 0.1-μm CML curve, and the hematite curve has a much smaller slope than the 0.35-μm CML and 0.2-μm silica curves. It should be noted, however, that the comparison between goethite and CML may not be fully justified because goethite's shape is also different.

The effects of both particle size and composition on concentration–turbidity correlations are due to the differences in their light scattering intensities. Increased slopes correspond to decreased light scattering intensity. This trend is clearly seen in Supplemental Fig. S1, where the measured specific turbidity values T_{m} (i.e., the light scattering intensity per unit mass of colloids), which have been used in previous studies (Foster et al., 1992; Gippel, 1995), are shown for different types of model colloids: Fe oxyhydroxides have larger T_{m} values than silica and CML particles, and hematite has a T_{m} value larger than all other particles. Furthermore, Supplemental Fig. S1 also shows the size effect on the light scattering intensity as indicated by decreased T_{m} values of CML with decreasing sizes.

The dependence of concentration–turbidity correlations on particle size and composition has been reported in other studies as well (Foster et al., 1992; Gippel, 1995). Our results indicate that the effect of size is more significant than the effect of composition. Moreover, the size effect is much more pronounced for nanosized particles, especially those with diameters <0.2 μm. This observation emphasizes the need to develop size-dependent concentration–turbidity correlations when quantification of nanoparticles in environmental samples is needed.

Concentration–Turbidity Correlations of Soil Samples

Measured concentration and turbidity values for the 37 soil samples are plotted along with linear regression lines in Fig. 2 for soil colloids in size fractions of 0.45 to 1.0, 0.1 to 0.45, and <0.1 μm. The mass concentrations of colloids correlate well with turbidity measurements, although there are variations among different soils. Overall, most data from the 37 soils can be fitted by the same curve within the size fractions of 0.45 to 1.0 and 0.1 to 0.45 μm but not for the <0.1-μm fraction. Similar to the observations with the model colloids, the concentration–turbidity curves of soil colloids are also size dependent, as indicated by the changes in slope with different size fractions. The slopes of the concentration–turbidity correlations are 0.77 ± 0.02 and 1.45 ± 0.03 for the 0.45- to 1.0- and 0.1- to 0.45-μm colloids, respectively. The size dependence is further reflected by the significant increases in T_{m} values with

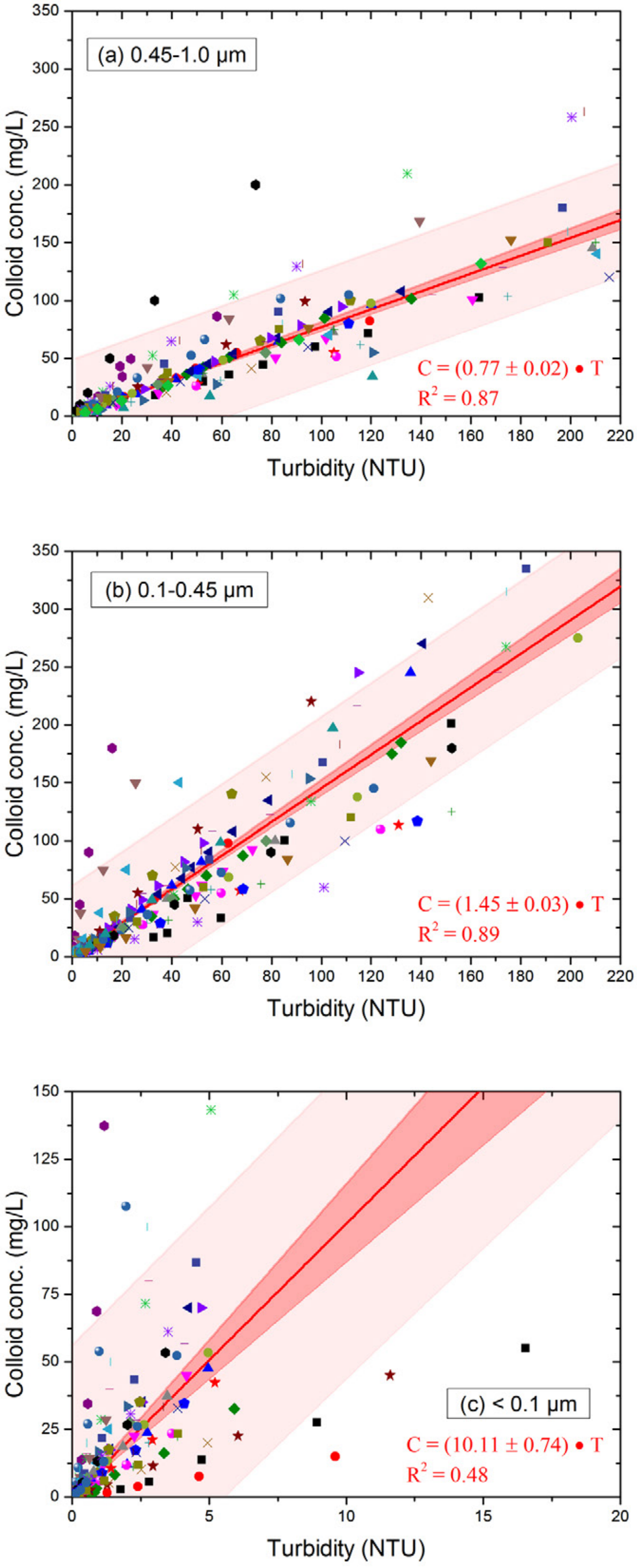

Fig. 2. Scatterplots and regression analyses between suspension turbidity (in nephelometric turbidity units, NTU) and mass concentration of soil colloids extracted from 37 soils for size-dependent correlations: (a) 0.45- to 1.0-, (b) 0.1- to 0.45-, and (c) <0.1-µm colloids; *C* and *T* in correlation equations represent colloid conc. (mg/L) and suspension turbidity (NTU), respectively, and R^2 is the coefficient of determination.

increasing colloid size ($p < 0.0001$ for one-way ANOVA with Tukey–Kramer HSD, Fig. 3). The size effect on turbidity measurements in environmental samples has been reported in previous studies on 0.45- to 100-µm sediments (Baker et al., 2001; Foster et al., 1992; Gippel, 1995; Landers and Sturm, 2013; Lewis, 1996; Schelde et al., 2002; Wass and Leeks, 1999). Our results further stress the importance of taking the size effect into consideration when turbidimetric quantification of colloids is used, especially for those <0.45 µm.

The effects of colloid composition on concentration–turbidity correlations were assessed by Pearson's correlation analyses between T_m and the chemical parameters of the soils, including free Fe oxide, clay, and organic C content (Fe%, Clay% and OC% in Supplemental Table S1). Supplemental Table S1 shows that the Fe and clay concentrations positively and organic C concentration are negatively correlated with T_m, but the statistical significances between T_m and these parameters were observed only for the <0.1-µm fraction ($p < 0.05$), not for size fractions of 0.45 to 1.0 and 0.1 to 0.45 µm. The limited composition effect within the 0.45- to 1.0- and 0.1- to 0.45-µm size fractions is probably due to the similarity in the refractive index (RI) values of the major mineral components of the colloids. In soil systems, the RI values of different clay minerals are similar, ranging from 1.5 to 1.6 (Supplemental Table S2), and thus significant shifting in concentration–turbidity correlations with increasing clay concentration is not expected. Similarly, although changes in the curve slopes are more likely in soils with higher Fe concentrations due to the considerably higher RI values of Fe oxyhydroxides (Supplemental Table S2), the Fe concentration in the 0.45- to 1.0- and 0.1- to 0.45-µm colloid fractions was not high enough to significantly increase the colloids' RI values. For example, Lafon et al. (2006) found that when the volumetric content of Fe oxides increased from 0 to 10.9%, RI values of aggregates only slightly increased

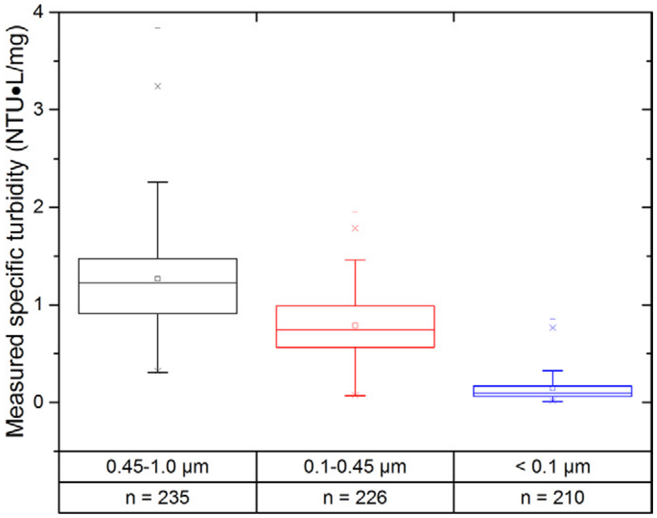

Fig. 3. Measured specific turbidity (T_m) of soil colloids from 37 soils in different size fractions; *n* is the number of samples and NTU is nephelometric turbidity units.

from ~1.5 to ~1.6, which are very similar to the RI of pure clay minerals (Supplemental Table S2).

The effect of organic matter (OM) on concentration–turbidity correlation is also limited: the correlations between organic C concentration and T_m values within the 0.45- to 1.0- and 0.1- to 0.45-µm fractions are not statistically significant (Supplemental Table S1). To further evaluate the effects of OM, we measured the turbidity values of concentrated OM suspensions prepared using Suwannee River humic acid (SRHA) at 75 and 150 mg/L C at <0.1-µm SRHA and found that they were both <0.2 NTU. Furthermore, the addition of 75 mg/L C SRHA to 1 and 43 mg/L CML suspensions only slightly decreased the turbidity of the CML from 4.5 to 4.2 NTU and 377.0 to 371.6 NTU, respectively (Supplemental Fig. S2). These observations confirm that the OM effect on turbidity measurement is negligible across a wide range of OM concentrations.

Compared with colloids in the size fractions of 0.45 to 1.0 and 0.1 to 0.45 µm, concentration–turbidity correlations of <0.1-µm colloids varied significantly and could not be fitted by a single correlation curve (Fig. 2c). The large variations are probably due to the significant differences in chemical composition within the <0.1-µm fraction. Unlike for the larger colloid fractions discussed above, the correlations between Fe concentration, clay concentration, and T_m are statistically significant at $p < 0.01$ and $p < 0.05$, respectively (Supplemental Table S1). These results imply that the relative importance of the composition effect increases as the specific turbidity decreases when the particle size approaches the nanosized range. Thus, concentration–turbidity correlations for nanoparticles could be more composition specific than their larger counterparts. On the other hand, it should be noted that both colloid concentration and turbidity are much lower in the <0.1-µm fraction than fractions of 0.45 to 1.0 and 0.1 to 0.45 µm, giving rise to larger measurement errors. In addition, as shown in Supplemental Fig. S2, the relative impacts of the OM effect also became more pronounced with decreasing colloid concentration and turbidity. All the factors discussed above could have contributed to the larger variations in the concentration–turbidity correlations, as shown in Fig. 2c.

Application of Correlation Curves to Field Samples

We applied the size-dependent concentration–turbidity correlations to the additionally collected water samples to calculate colloid concentrations within the size fractions of 0.1 to 0.45 and 0.45 to 1.0 µm, then compared the calculated values with gravimetrically measured concentrations (detailed method procedure is provided in the supplemental material). As shown in Fig. 4, the calculated values agreed well with the measured concentrations, with most data falling on the 1:1 line and only a few outliers. Calculated/measured concentration ratios are summarized in Supplemental Fig. S3, most ranging from 0.95 to 1.26. The ratios suggest that predictions from the size-dependent concentration–turbidity correlations are reliable for most samples, although there could be exceptions.

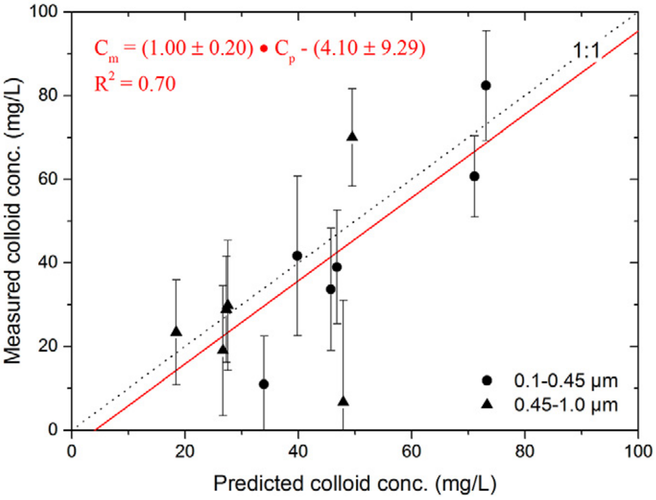

Fig. 4. Regression analysis between measured and calculated colloid concentrations for field samples; C_m and C_p in correlation equations represent measured and calculated colloid concentrations (mg/L), respectively, and R^2 is the coefficient of determination.

Additionally, the colloid concentrations of these samples were separately calculated from the correlation curves for the 0.1- to 0.45- and 0.45- to 1.0-µm colloids (Fig. 2a and 2b) and a "combined" curve, i.e., the curve of <1.0 µm (Fig. 5, a curve typically used) and compared. The size-dependent correlations provide more accurate estimation and less uncertainty in colloid concentrations than the combined curve, as reflected by smaller absolute and relative errors (Table 2) and lower calculated/measured ratios

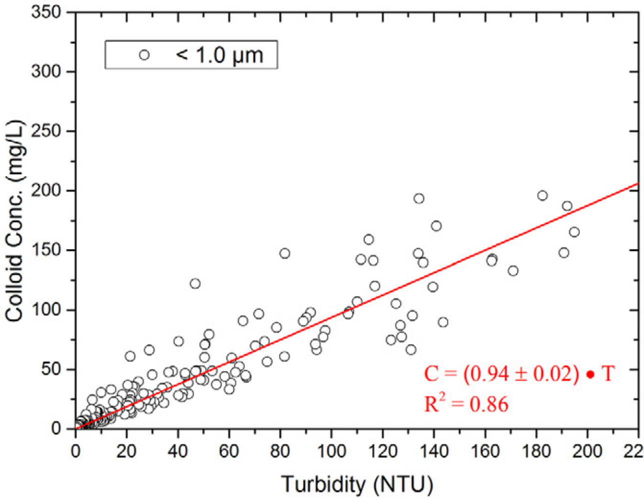

Fig. 5. Scatterplots and regression analyses between suspension turbidity and mass concentration of soil colloids extracted from 37 soils for "combined" correlations: <1.0-µm colloids; C and T in correlation equations represent colloid concentration (mg/L) and suspension turbidity (nephelometric turbidity units, NTU), respectively, and R^2 is the coefficient of determination.

Table 2. Comparison between calculated and measured colloid concentrations from size-dependent correlations (SDC) and “combined” correlation (CBC) and error analysis.

Size	Measured colloid conc.	Calculated colloid conc.		Absolute error†		Relative error‡	
		SDC	CBC	SDC	CBC	SDC	CBC
	mg/L						
0.1–0.45 µm	70.7 ± 13.4	73.1 ± 1.5	47.2 ± 2.0	2.4	23.5	0.0	0.3
	38.3 ± 13.4	45.7 ± 0.9	29.5 ± 1.3	7.4	8.8	0.2	0.2
	73.4 ± 9.5	71.1 ± 1.5	45.9 ± 2.0	2.3	27.5	0.0	0.4
	44.9 ± 13.6	46.8 ± 1.0	30.2 ± 1.3	1.9	14.6	0.0	0.3
	41.7 ± 19.1	39.8 ± 0.8	25.7 ± 1.1	1.9	16.0	0.0	0.4
	12.2 ± 5.6	33.9 ± 0.7	21.9 ± 0.9	21.7	9.7	1.8	0.8
All 0.1–0.45 µm§	46.9	51.8	33.4	4.9	13.5	0.1	0.3
0.45–1.0 µm	18.4 ± 24.4	47.9 ± 1.2	58.4 ± 2.5	29.5	40.0	1.6	2.2
	30.5 ± 15.2	27.5 ± 0.7	33.5 ± 1.4	3.0	3.0	0.1	0.1
	57.4 ± 11.4	49.5 ± 1.3	60.3 ± 2.6	7.9	2.9	0.1	0.1
	24.7 ± 12.7	27.3 ± 0.7	33.2 ± 1.4	2.6	8.5	0.1	0.3
	20.1 ± 14.2	26.7 ± 0.7	32.5 ± 1.4	6.6	12.4	0.3	0.6
	24.2 ± 3.3	18.4 ± 0.5	22.4 ± 1.0	5.8	1.8	0.2	0.1
All 0.45–1.0 µm§	29.2	32.9	40.0	3.7	10.8	0.1	0.4

† Calculated from the absolute difference between the mean values of calculated and measured colloid concentration.

‡ Calculated from the absolute error divided by the measured colloid concentration.

§ Only average values are provided for measured and calculated colloid concentrations.

(Supplemental Fig. S3). This implies that size-dependent correlations should be promoted to quantify colloid concentrations in environmental samples.

Despite the large number of soil samples used in this study to develop the size-dependent concentration–turbidity correlations for colloid quantification, it should be noted that caution must be used when applying these relationships. Because of the extremely heterogeneous nature of soil and sediment materials, exceptions are expected to exist (e.g., when sample compositions are significantly different from the soils used in this study) where these correlations may not apply. To alleviate errors in colloid quantification, potential users are encouraged to verify the correlations using their own samples whenever possible. In addition, more measurements of size-dependent concentration–turbidity correlations for colloids prepared from additional soils would reduce uncertainty and provide more confidence in applying these correlations for quick and accurate quantification of colloids in field samples.

Conclusions

In this study, we tested the reliability of using turbidimetric measurements to quantify colloid concentrations in aquatic environmental samples and developed size-dependent turbidity–concentration correlations for three colloidal size fractions (0.45–1.0, 0.1–0.45, and <0.1 µm) based on measurements from a large number of soil samples. We demonstrated that particle size is the dominant factor affecting the correlation between turbidity and colloid concentration, while the effects of particle composition and OM are largely negligible. The size-dependent concentration–turbidity correlations provide more accurate estimations when tested against gravimetric measurements using field samples compared with the combined curve for <1.0-µm colloids, which is more commonly used. The relatively insignificant particle-composition effect indicates the practically “universal” applicability of the reported correlations. In addition, the correlations, for the first time, allow quantification of colloids in different size fractions in environmental samples, especially colloids that are <0.45 µm, which are traditionally considered as part of the dissolved phase and hence underestimated. This would enhance our capability to more accurately quantify the colloidal pools in natural systems. Furthermore, size-dependent correlations provide size-specific quantification of colloids within the fraction of <1.0 µm, thus improving our understanding of the biogeochemical cycling of constituents involving a colloid contribution, especially if the contribution is colloid size dependent. For example, colloids of varying sizes have different surface areas available for the constituents to sorb on and they differ in mobility. The colloid quantification method developed in our study will enhance our capability to quantify colloidal pools in natural systems, especially for <0.45-µm fractions, and therefore provides a more accurate assessment of the mobility of colloid-associated constituents, such as nutrients, contaminants, and trace elements.

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