

Colloid Mobilization and Seasonal Variability in a Semiarid Headwater Stream

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Abstract

Colloids can be important vectors for the transport of contaminants in the environment, but little is known about colloid mobilization at the watershed scale. We present colloid concentration, composition, and flux data over a large range of hydrologic conditions from a small watershed (Gordon Gulch) in the foothills of the Colorado Front Range. Colloids, consisting predominantly of Si, Fe, and Al, were present in most stream samples but were not detected in groundwater samples. Mineralogical and morphological analysis indicated that the colloids were composed of kaolinite and illite clays with lesser amounts of amorphous Fe-hydroxides. Although colloid composition remained relatively constant over the sampled flow conditions, colloid concentrations varied considerably and increased as ionic strength of stream water decreased. The highest concentrations occurred during precipitation events after extended dry periods. These observations are consistent with laboratory studies that have shown colloids can be mobilized by decreases in pore-water ionic strength, which likely occurs during precipitation events. Colloidal particles constituted 30 to 35% of the Si mass flux and 93 to 97% of the Fe and Al mass fluxes in the <0.45- μm fraction in the stream. Colloids are therefore a significant and often overlooked component of mass fluxes whose temporal variations may yield insight into hydrologic flowpaths in this semiarid catchment.

Core Ideas

- Riverine colloids were quantified across a wide range of flow and antecedent moisture conditions.
- Colloids were dominated by kaolinite and illite clays with lesser amounts of amorphous iron.
- Colloid composition was constant across wide ranges in flow.
- Mobilization occurred after dry periods and increased with decreasing stream ionic strength.

COLLOIDS affect the fate and transport of contaminants in the environment, including organic compounds, trace metals, radionuclides, bacteria, and viruses (Corapcioglu and Jiang, 1993; de Jonge et al., 2004; Kanti Sen and Khilar, 2006; Kretzschmar and Schafer, 2005; Kretzschmar et al., 1999; Ryan and Elimelech, 1996). In river systems, colloids have been shown to contribute substantially to watershed fluxes of macronutrients from continents to oceans (Andersson et al., 2006; Dahlqvist et al., 2007; Jarvie et al., 2012). Because trace metals and rare earth elements adsorb to colloidal particles, colloiddally bound metals can constitute the majority of the riverine flux (Kimball et al., 1995; Pokrovsky and Schott, 2002). Colloids typically constitute particles in the 1-nm to 10- μm size fraction (Kanti Sen and Khilar, 2006), but many studies operationally define dissolved constituents as passing through a <0.45- μm filter, which can include small colloidal particles. However, there are relatively few studies directly measuring riverine colloids (Jarvie et al., 2012), despite their role as contaminant and macronutrient vectors. In contrast, there is a large body of literature on colloid mobilization in soil and groundwater systems (DeNovio et al., 2004; Kanti Sen and Khilar, 2006; McCarthy and Zachara, 1989; Ryan and Elimelech, 1996), and it has been shown from laboratory and small-scale field studies that hydrologic and chemical perturbations can substantially affect the mobility of colloids. In surface-water systems, it has been noted that the composition and concentration of colloids can vary in response to hydrologic events such as storm flow (Grout et al., 1999) or snowmelt (Dahlqvist et al., 2007), but few data exist on riverine colloids over a wide range of flow conditions (Jarvie et al., 2012). There is a need to examine riverine colloids in the context of changing hydrologic and chemical conditions to begin to understand the processes governing colloid mobilization at the watershed scale.

Colloids can adhere to pore or fracture surfaces due to the net effect of double-layer repulsion or attraction, London-van der Waals attractions, and other short-range forces (Ryan and Elimelech, 1996). Interactions between colloids and surfaces due to these forces can be described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Derjaguin and Landau, 1941).

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J. Environ. Qual. 46:88–95 (2017)

doi:10.2134/jeq2016.07.0268

Received 20 July 2016.

Accepted 1 Nov. 2016.

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Abbreviations: CZO, Boulder Creek Critical Zone Observatory; DLVO, Derjaguin–Landau–Verwey–Overbeek; ET, evapotranspiration; ICP–OES, inductively coupled plasma optical emission spectroscopy; IS, ionic strength; XRD, X-ray diffraction.

Colloids can detach from surfaces and be mobilized due to hydrologic or chemical perturbations in soil or aquifer systems. In the case of hydrologically induced colloid mobilization, forces associated with increased flow velocity through a pore or a fracture can exceed the binding forces described by DLVO theory and detach the colloid from the surface (Bergendahl and Grasso, 2000). Colloid mobilization in soils can occur during precipitation events due to increased flow velocities (Kaplan et al., 1993; Rousseau et al., 2004) or in aquifer systems due to pumping of groundwater (Ryan and Elimelech, 1996).

Chemically induced colloid release is a primary process controlling colloid mobilization in soil and groundwater systems and can occur due to changes in solution pH and ionic strength (Hiemenz and Rajagopalan, 1997; McCarthy and Degueldre, 1993). Ionic strength (IS) control generally dominates, except when pH changes span multiple pH units (Grolimund and Borkovec, 1999; Roy and Dzombak, 1997; Ryan and Elimelech, 1996). Solution IS has been shown in laboratory column experiments to be a primary mechanism of chemically induced colloid mobilization (Ryan and Gschwend, 1994). A decrease in solution IS can mobilize colloids from surfaces by expanding the electrostatic double layers around colloids and surfaces (Hunter, 1981), causing a reduction in the attractive forces.

Colloid mobilization has been studied through laboratory column experiments under ideal, saturated conditions, where the column is filled with homogeneous material and flow velocity through the column is relatively constant. However, more recent work has focused on nonideal, unsaturated conditions that are more analogous to field conditions (DeNovio et al., 2004). Laboratory and small-scale field studies using intact soil cores or simulated rainfall have shown that transience in flow conditions can facilitate colloid release. Soil drying can increase in situ colloid generation through weakening of the soil matrix (Majdalani et al., 2008), but the mobility of colloids has been found to generally decrease with decreasing water content due to the tendency of colloids to adhere to air–water interfaces in pores (Saier et al., 2003; Torkzaban et al., 2006; Wan and Wilson, 1994). However, colloids can be mobilized during infiltration events through dry soils when air–water interfaces are destroyed by the wetting front, resulting in a pulse of mobile colloids in soil column effluent (Bradford and Torkzaban, 2015; Cheng and Saier, 2009). Macropore flow has also been shown to enhance colloid mobility (Laegdsmand et al., 1999; Wang et al., 2014), and macropore flow is often enhanced by infiltration through dry soils (Beven and Germann, 1982). These processes typically exhibit spatial and temporal variability in natural systems and encompass many small-scale physicochemical factors influencing colloid transport, making detailed process descriptions difficult at the hillslope or watershed scale. Nevertheless, there is a need to characterize colloid transport in complex systems to begin to understand colloid mobilization in the environment (McCarthy and McKay, 2004).

In this study we present colloid concentration, composition, and flux data from a small headwater catchment collected weekly over a 2-yr period with large changes in hydrologic conditions. The goal of this study is to evaluate stream colloid mobilization in the context of hydrologic and chemical perturbations in the stream to better understand the processes facilitating colloid mobilization at the watershed scale.

Materials and Methods

Site Description

This study was conducted in the headwaters of Gordon Gulch, a 0.95-km² catchment located about 20 km west of Boulder, CO, within the Boulder Creek Critical Zone Observatory (CZO) (Anderson et al., 2012). The CZO is a network of 10 field observatories spanning a range of climatic, ecologic, and geologic environments focused on the interactions between physical, chemical, and biological processes on the Earth's surface. Gordon Gulch ranges in elevation from 2588 m on the valley floor to 2734 m at the ridgetops and drains the east side of the Colorado Front Range. The climate is semiarid, with a mean annual air temperature of 6.9°C and mean annual precipitation of 506 mm for the period 1994 to 2014 (site CO98) (NADP, 2015). Peak discharge in the stream generally occurs in spring, driven by melting of the discontinuous snowpack and spring rain storms (Anderson et al., 2014). Gordon Gulch emerges as a small perennial stream in a willow-aspen stand below a montane meadow and flows 1 km to the gaging station. There are no residential developments in the watershed, but some dirt roads are present near the top of the basin. The watershed primarily is underlain by Precambrian biotite gneiss (Gable, 1996) and has developed a weathered profile 8 to 30 m thick (Befus et al., 2011). Soils are predominantly Alfisols on north-facing slopes and Mollisols on south-facing slopes (Dethier et al., 2012). Saprolite is typically found at about 40 cm depth (Diek et al., 2014; Hinckley et al., 2014), and saprolite and soils show relatively little geochemical alteration compared with the underlying bedrock (Anderson et al., 2014).

Hydrologic Monitoring and Sample Collection

During 2011 and 2012, streamflow data were collected at a permanent stream gauge at 10-min intervals. Discharge was computed using a stage–discharge rating curve based on numerous manual discharge measurements throughout the year (Rantz, 1982). Considerable uncertainty in manual measurements and low sensitivity of our pressure transducer during low-flow periods resulted in low confidence in the stage–discharge relationship under low-flow conditions. As a consequence, we consider discharge below 3 L s^{−1} as below our measurement range. Precipitation data were obtained from a nearby National Atmospheric Deposition Program site located 2.8 km south of the watershed at similar (2524 m) elevation (site CO94) (NADP, 2015).

Groundwater levels were monitored in three wells located up-valley from the stream gauge. Two wells are located in opposing valley slope positions (Wells 1 and 6), about 100 m from the channel, and one in a valley floor position (Well 2), about 20 m from the channel. Water levels were measured at 10-min intervals using pressure transducers and intermittently verified using manual depth to water measurements. All pressure transducers were corrected for temperature and barometric pressure (Freeman et al., 2004).

Water-quality samples were collected weekly at the stream gauge using 1-L high-density polyethylene bottles. Groundwater wells were sampled approximately monthly and were sampled after bailing or pumping the well until the water temperature stabilized. Groundwater samples were then pumped into 1-L high-density polyethylene collection bottles using a peristaltic pump. All water samples were filtered through 0.45-μm membrane filters (MF-Millipore) using a vacuum pump within 72 h of sample

collection. Water samples were stored at 4°C to maintain sample integrity until filtering. Streamwater samples were analyzed for concentrations of major cations (Ca, Mg, Na, and K) and anions (Cl, SO₄, and NO₃), Fe, Al, and Si in the laboratory. Major anions were analyzed by ion chromatography at the Boulder Creek CZO laboratory, and major cations, Fe, Al, and silica were analyzed by inductively coupled plasma optical emission spectroscopy (ICP–OES) at the Laboratory for Environmental and Geological Sciences, Boulder, CO. Groundwater samples were only analyzed for major cations, anions, and Si, following methods described for streamwater samples. Alkalinity was determined in the Boulder Creek CZO laboratory by Gran titration (Gran, 1952).

Silica and Colloid Analysis

As described above, all filtered water samples were analyzed for total Si by ICP–OES, but stream samples also were analyzed for reactive, monomeric SiO₂ using the molybdate blue method (Leo and Leen, 2013). Additionally, an aliquot from a subset of samples collected in 2011 was centrifuged for 4.5 h at 8000 rpm using a head with initial and final axes of rotation of 16 and 24 cm, respectively, to remove colloidal particles >0.02 μm. After centrifugation, the supernatant was decanted off and analyzed for major cations, Si, Fe, and Al by ICP–OES.

One large-volume streamwater sample and one soil sample were collected in October 2015 to concentrate colloidal material for characterization using X-ray diffraction (XRD) and scanning electron microscopy. A 12-L streamwater sample was filtered using high-capacity 0.45-μm Geotech disposa-a-filters. The filtrate was then centrifuged, and the centrifuged pellets were aggregated for XRD analysis. Colloids also were isolated from the soil sample. Soil was augured using a bucket auger until refusal on saprolite at 50 cm at a location about 200 m upstream from the gauge and about 10 m from the channel. The aggregated soil sample was mixed with 4 L of deionized water on a shaker table for 1 h and then filtered and centrifuged as described above. Colloids isolated from the stream and soil samples were treated with ethylene glycol and analyzed by XRD at the Cornell Center for Materials Research, New York. A split of the colloids isolated from both samples was examined using a FEI Quanta 450 FEG Scanning Electron Microscope with an EDAX Energy Dispersive Spectroscopy instrument at the USGS Denver Microbeam Laboratory.

Definitions of Dissolved and Colloidal Fractions

Our processing and analysis of streamwater samples yielded three operationally defined element fractions: dissolved plus colloidal (<0.45 μm), dissolved (<0.02 μm), and molybdate-blue reactive (truly dissolved monomeric Si). The dissolved plus colloidal fraction, hereafter referred to as “filtered,” was determined by ICP–OES analysis of 0.45-μm filtered samples. The 0.45-μm filter pore size was chosen because a <0.45-μm size cutoff is commonly used to define dissolved constituents in rivers. The dissolved fraction, hereafter referred to as “centrifuged,” was determined by ICP–OES analysis of the supernatant from samples that had been filtered and centrifuged to remove particles >0.02 μm. The ICP–OES analysis uses a high-temperature plasma to ionize the sample and is a measure of the dissolved and colloidal element concentration in water samples. Thus, the difference in concentration between the filtered and centrifuged fractions determined by ICP–OES can be used as an estimate of the colloidal fraction.

The molybdate-blue reactive fraction, hereafter referred to as “colorimetric Si,” only pertains to Si and was determined by the molybdate-blue colorimetric analysis of 0.45-μm filtered samples. The colorimetric Si fraction is comprised of only molybdate-blue-reactive, monomeric Si because the analysis does not detect colloidal forms of Si (Leo and Leen, 2013). Groundwater samples were only analyzed for the filtered and centrifuged fractions. The major cation, Fe, Al, and Si concentrations of the colloidal fraction in samples collected in 2011 were determined by the difference between the filtered and centrifuged fractions. Exclusion of some particles smaller than the 0.45-μm pore size of the filters can occur due to pore clogging (Morrison and Benoit, 2001), and thus the calculated colloidal concentrations are likely a low estimate. Additionally, colloidal particles >0.45 μm removed during sample filtration were not quantified as part of this study, and thus only colloids between 0.02 and 0.45 μm are discussed.

Results

Hydrology

The peak daily mean discharge in 2011 of 59.3 L s⁻¹ occurred in May, driven by melting of an above-average snowpack (142% of May average) (NRCS, 2016) and spring rain events (Fig. 1). Discharge then declined through early summer, punctuated by episodic increases in response to summer rain events, before reaching relatively stable baseflow conditions from late July through early October. In 2012, there was little spring runoff owing to a below-average snowpack (22% of May average) (NRCS, 2016)

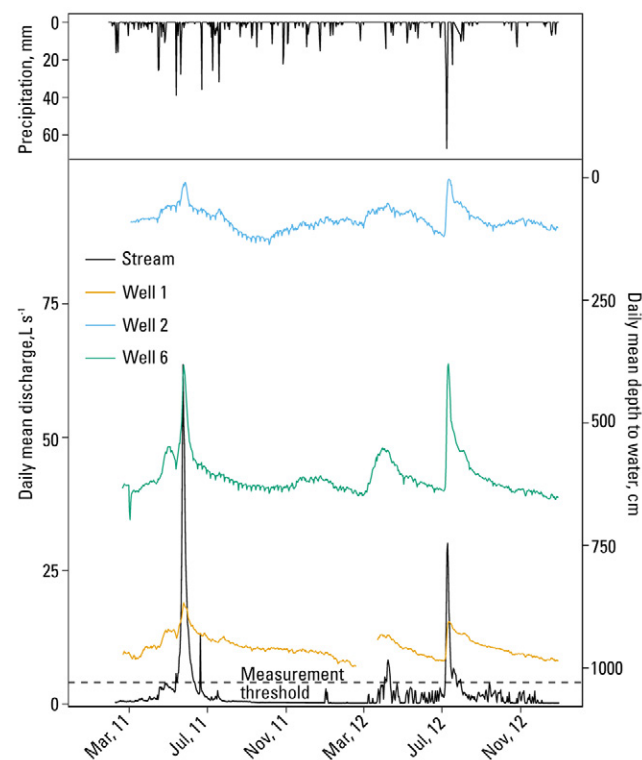


Fig. 1. Time series of daily mean discharge (left axis), daily mean depth to water (right axis), and precipitation, 2011 and 2012. Precipitation is measured in total mm accumulated over the event duration. Precipitation data were not available during September 2012. Dotted line represents the threshold below which discharge values are taken as estimated. Precipitation was measured at the Sugarloaf CO94 NADP site (NADP, 2015).

and few precipitation events in May. Peak discharge in 2012 of 28 L s⁻¹ occurred in early July in response to a series of convective rainstorms that occurred during 3 through 10 July. Discharge declined through August to baseflow levels in September. Groundwater levels generally mirrored patterns in the stream hydrograph (Fig. 1). In all three wells, the water table rose during high-flow conditions, fell during low-flow conditions, and was at a minimum during summer low-flow conditions. Groundwater levels rose slightly in Wells 1 and 2 during winter low-flow conditions. Depth to water ranged from 910 to 380 cm below land surface at the hill-slope wells and from 120 cm below land surface to at or near the land surface in the valley floor well (Fig. 1).

Partitioning of Elements between Dissolved and Colloidal Fractions

Colloidal material was present in the majority of streamwater samples and was composed primarily of Si, Fe, and Al (only 2011 samples analyzed for Fe and Al). Comparison of filtered and centrifuged fractions revealed significantly higher median concentrations (Mann–Whitney test, $p < 0.001$) of Si, Fe, and Al in the filtered fraction than in the centrifuged fraction (Fig. 2a). Median Si concentrations decreased by about 30% between filtered and centrifuged fractions, indicating a large portion of Si is present in the dissolved form. Iron and Al were particularly abundant in a colloidal form, as shown by median Fe and Al concentrations decreasing by more than an order of magnitude between filtered and centrifuged fractions (Fig. 2a). In contrast, there were no significant differences (Mann–Whitney test, $p > 0.05$) in median concentrations of major cations between filtered and centrifuged fractions, indicating these elements reside primarily in the dissolved form. However, filtered Mg concentrations were slightly higher than centrifuged concentrations in many samples, but the differences were not significant (Mann–Whitney test, $p > 0.05$). Silica dominated the colloidal fraction, followed by Al and Fe, with molar ratios of approximately 10:7:1.5, respectively. Colloidal particles did not appear to be present in groundwater samples because

there were no significant differences (Mann–Whitney test; $p > 0.05$) in Si between the filtered and centrifuged fractions (Fig. 2b).

The difference between the Si concentrations in the filtered and colorimetric Si fractions could be used as an estimate of colloidal Si concentrations in water samples because the molybdate-blue method is not sensitive to colloidal Si. To test this hypothesis, the Si concentrations in the filtered and centrifuged fractions were compared with the Si concentrations in the colorimetric Si fraction of samples collected in 2011 (Fig. 3). Indeed, Si concentrations were nearly identical between the centrifuged and colorimetric fractions, and there was no significant difference (Mann–Whitney test; $p > 0.05$) between the median concentrations of the two fractions. These results indicate that the difference in Si concentration between the filtered and colorimetric fractions can be used as a measure of colloidal Si concentrations in filtered water samples. Additionally, these results indicate that there was little or no colloidal material in the $<0.02\text{-}\mu\text{m}$ size fraction, which would not have been removed by centrifugation. Colloidal Si concentrations in stream samples collected in 2011 and 2012 were taken as the difference between the filtered and colorimetric fractions.

X-Ray Diffraction and Scanning Electron Microscopy Analysis of Colloids

X-ray diffraction and scanning electron microscopy analysis of colloids extracted from both the large-volume stream sample and the soil leachate sample indicate that the colloids are primarily a mixture of kaolinite and illite with lesser amounts of Fe-hydroxides. This is consistent with the Si/Al/Fe molar ratio of 10:7:1.5 and with the low major-cation concentrations in the centrifuged fraction compared with the filtered fraction. Additionally, the presence of illite may explain the slightly higher Mg concentrations in the filtered fraction of some samples (Fig. 2b). Imaging of the colloidal particles by scanning electron microscopy shows many discrete, angular particles, indicative of a crystalline clay morphology rather than an amorphous gel (Fig. 4). A few particles are dark (denser) in the scanning electron microscopy images

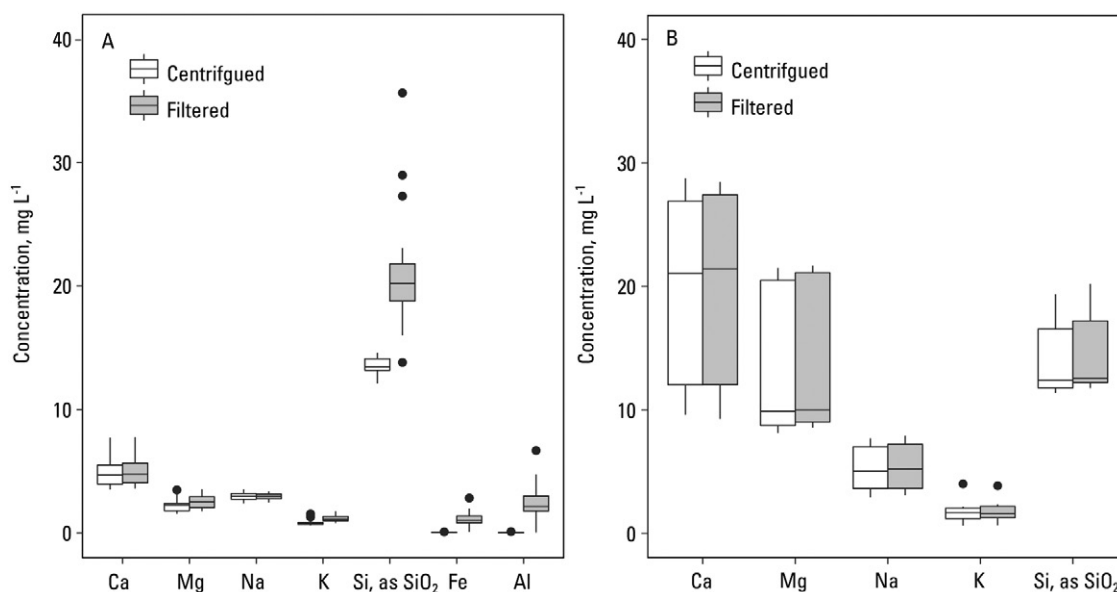


Fig. 2. Boxplots of element concentrations for filtered and centrifuged fractions in (A) stream samples and (B) groundwater samples collected in 2011. The box of the boxplot encompasses the 25th and 75th percentiles of the data, and the whiskers extend to the 10th and 90th percentiles. Points are samples that lie beyond the 10th and 90th percentiles. Numbers above each boxplot indicate the number of samples.

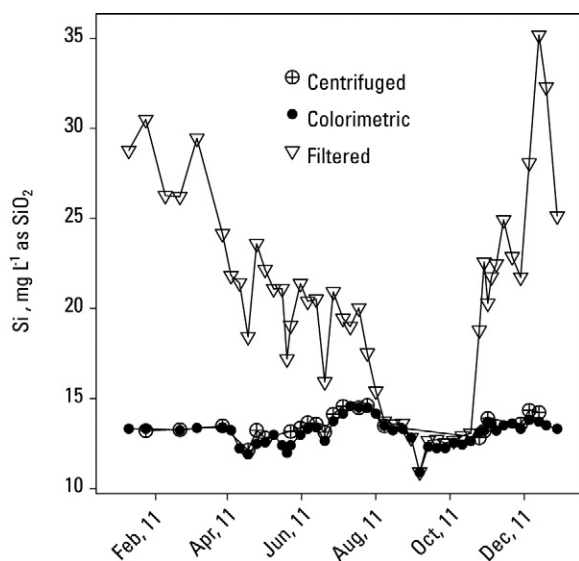


Fig. 3. Time series of filtered, centrifuged, and colorimetric silica concentrations in stream samples in 2011.

and lack angular shapes, suggesting they probably are amorphous Fe-hydroxides, which is consistent with higher concentrations of Fe in the filtered than the centrifuged fractions.

Discussion

Dissolved and Colloidal Fluxes of Si, Al, and Fe

The dissolved and colloidal fluxes were estimated for Si in 2011 to 2012 and for Fe and Al in 2011 and revealed that the $<0.45\text{-}\mu\text{m}$ colloidal fraction constituted a substantial portion of the total (dissolved + colloidal) stream flux for all three elements (Table 1). Loads were estimated by multiplying daily streamflow by the daily dissolved and colloidal concentration of each element. Because water chemistry samples were collected on a weekly basis, a linear interpolation was used to estimate daily concentration values between sampling events. The colloidal Si flux accounted for 36 and 32% of the total stream flux in 2011 and 2012, respectively. The colloidal flux accounted for over 90% of the total stream flux for Fe and Al in 2011, consistent with the

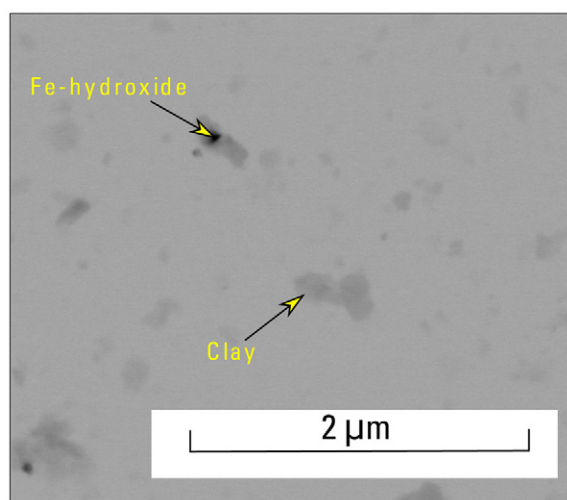


Fig. 4. Scanning electron microscopy image of colloidal particles isolated from the large-volume stream sample. Darker regions indicate higher density material.

strong partitioning of Fe and Al into the colloidal rather than the dissolved fraction observed in this study.

The substantial contributions of colloidal particles to the Si, Fe, and Al flux may have important implications for nutrient export from the watershed. Silica is an important macronutrient for diatoms in streams and oceans, and silica consumption for diatom growth is a primary mechanism regulating global atmospheric CO_2 concentrations (Ragueneau et al., 2000). Dissolved silicic acid is the primary form of silica utilized by marine diatoms (Amo and Brzezinski, 1999), and studies of water chemistry often define the dissolved fraction as that which passes through a $0.45\text{-}\mu\text{m}$ filter. About one third of the Si flux in the $<0.45\text{-}\mu\text{m}$ fraction measured in this study is associated with the colloidal fraction rather than with the dissolved Si. Thus, studies analyzing Si by ICP-OES in an operationally defined dissolved Si fraction $<0.45\text{ }\mu\text{m}$ may substantially overestimate the dissolved Si flux if colloidal Si is present, which could influence calculated Si and C budgets. However, colloid generation and mobilization processes occurring in this small headwater stream may not be analogous to larger river systems. Measurements of dissolved and colloidal Si in larger river systems over varying flow regimes is needed to assess the importance of colloidal Si fluxes at larger scales.

Seasonal Variations in Colloid Composition and Concentration

The composition of the colloidal particles in streams has been observed to vary with changing hydrologic conditions. Grout et al. (1999) noted variations in the organic C, Si, Fe, and Al content of colloids during an urban stormflow event, which the authors suggested could be due to changing colloid sources or hydrologic flowpaths. Seasonal variations in colloid composition have also been observed in boreal river systems, driven primarily by changing flowpaths during spring flood events (Andersson et al., 2006; Dahlqvist et al., 2007). In contrast, the relative Si, Fe, and Al composition of the colloids measured during this study varied by less than 1% throughout the year despite large variations in flow. Additionally, the concentrations of Si, Fe, and Al in the colloidal fraction were highly correlated ($n = 20$, $r = 0.99$ for all correlations; $p < 0.001$), suggesting a common colloid source or mechanism of mobilization for these elements.

Because colloids were not detected in groundwater samples, the source of the colloids appears to be from shallow flowpaths through the soil profile. This conclusion is supported by the chemistry of colloids extracted from the soil leachate which had

Table 1. Calculated loads for Si, Fe, and Al in dissolved and colloidal fractions. The dissolved Si fraction is taken as the colorimetric Si concentration. The colloidal Si fraction is calculated from the difference between filtered and colorimetric Si concentrations. The dissolved Fe and Al fractions are taken as the centrifuged Fe and Al concentrations. The colloidal Fe and Al fractions are calculated from the difference between filtered and centrifuged Fe and Al concentrations, respectively.

Year	Dissolved			Colloidal			Colloidal load (percent of total load)		
	Si†	Fe	Al	Si†	Fe	Al	Si	Fe	Al
kg yr ⁻¹									
2011	764	4.80	4.51	435	62.8	134	36	92	97
2012	631	—†	—	304	—	—	32	—	—

† As SiO_2 .

‡ Not analyzed.

a Si/Al/Fe molar ratio nearly identical to the stream colloids and also exhibited similar morphology when examined by scanning electron microscopy. The median Si/Al/Fe ratio of stream samples was 10:7:1.5, compared with a Si/Al/Fe ratio of 10:6.5:1.5 for soil colloids, which is consistent with the mixed kaolinite-illite composition determined by XRD.

Colloid concentrations varied considerably over the year (Fig. 5), with the highest concentrations during the fall and winter, decreasing concentrations through spring, and the lowest concentrations during summer baseflow conditions. This pattern was most evident in 2011 when baseflow conditions extended from late July to early October and colloid concentrations were at or near zero (Fig. 5). The low colloid concentrations in streamwater during baseflow are likely due to a shift from shallower flowpaths through soil during wetter conditions to deeper groundwater sources during dry conditions. In 2012, colloid concentrations declined markedly in late spring and reached a minimum in late June. However, in contrast to 2011, a period of extended summer storms produced a discharge peak in July, with a concomitant peak in colloid concentrations (Fig. 5).

Mechanisms of Colloid Mobilization

In both years, colloid concentrations were at a minimum during summer baseflow conditions when IS was increasing (Fig. 5). Colloid concentrations rapidly increased in the stream at the end of the summer baseflow period in fall 2011 and July 2012, coinciding with a decrease from high to low IS. Decreases in IS often occur in watershed systems during rain or snowmelt events due to the influx of dilute meteoric water, and the calculated IS of Gordon Gulch stream samples declined substantially in response to precipitation events in the fall of 2011 and in the

summer of 2012 (Fig. 5). This behavior is consistent with DLVO theory, which predicts that decreases in IS will increase repulsive forces between colloids and surfaces and therefore facilitate colloid dispersion and mobilization (Khilar et al., 1990; Ryan and Gschwend, 1994). However, precipitation events during summer baseflow conditions in 2011 did not produce a marked change in IS or colloid concentration. It is likely these small rain events were not substantial enough to overcome the higher evapotranspiration (ET) demand during the summer months, resulting in limited soil drainage to the stream channel.

Ionic strength remained low through the winter low-flow period in 2011 and 2012, and colloid concentrations were elevated. Ionic strength decreased further during spring high-flow conditions, particularly in 2011 (Fig. 5). However, no corresponding peak in colloid concentration was observed during the spring discharge peak in 2011 despite minimum values of IS. Dilution by the large influx of meteoric water may explain the lack of increase in colloid concentrations during spring high-flow conditions in 2011. However, the large increase in colloid concentrations during summer high-flow in 2012 suggests dilution alone cannot explain the low colloid concentrations during spring high-flow in 2011. A lack of soil drying during the winter months may be responsible for the declining colloid concentrations during spring high-flow conditions. Spikes in colloid concentrations during initial infiltration events after dry periods have been observed in laboratory column experiments. Additionally, propagation of wetting fronts through dry soils may further enhance colloid mobilization. This phenomenon has been attributed to colloid generation by physical processes, such as weakening of the soil matrix by capillary stresses during drying (Majdalani et al., 2008), increased colloid transport by macropore flow during infiltration events through dry soils (Mohanty et al., 2015), and mobilization of colloids adhered to air-water interfaces that are destroyed during soil wetting (Bradford and Torkzaban, 2015; Cheng and Saiers, 2009). Episodic snowmelt events during the winter and decreased ET likely limit the amount of soil drying, which probably limits colloid generation and mobilization during spring high-flow conditions in 2011 compared with summer high-flow conditions in 2012.

Soil colloids could also be mobilized by surface runoff (Bradford et al., 2015; Turner et al., 2004). However, surface runoff was not observed in the watershed during the study period and also has not been observed during snowmelt infiltration and modeling experiments by Hinckley et al. (2014). Another possible source of elevated colloid concentrations is resuspension of colloids trapped in streambed sediments. Colloids can accumulate in streambed sediments through settling and filtration (Packman et al., 2000) and could possibly be resuspended during precipitation events if conditions are favorable for detachment, such as increased streamflow velocities or decreased IS. Physical resuspension of colloids in the streambed sediments is unlikely given the high colloid concentrations observed during low-flow conditions in the fall and winter when instream velocities are low. The abrupt changes in stream IS in the fall and winter may facilitate colloid mobilization from the streambed sediments. However, it is unlikely substantial amounts of colloidal particles would be deposited in the streambed during the summer baseflow period because streamflow is composed primarily of

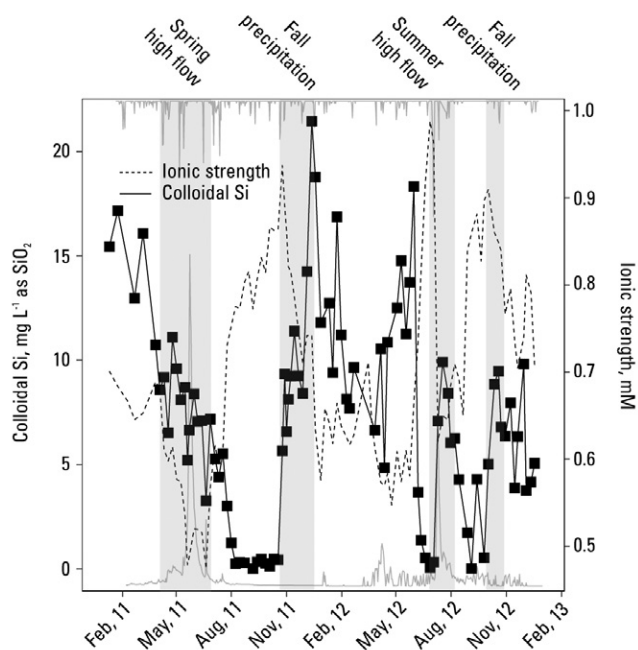


Fig. 5. Time series of colloidal silica concentration (left axis) and ionic strength (right axis) of stream samples collected in 2011 and 2012. Traces of precipitation and stream discharge are shown in gray at the top and bottom of the figure, respectively. Shaded regions indicate different hydrologic conditions. Colloidal silica was taken as the difference between silica concentrations in the centrifuged and colorimetric fractions of stream samples.

groundwater during baseflow conditions and colloids were not detected in groundwater samples.

Decreases in solution IS are known to enhance colloid mobility, but the patterns observed in this study between IS and colloid concentrations can also be interpreted in the context of the watershed hydrologic regime. Rising IS occurs in summer when there is little precipitation, ET rates are higher, and the watershed soils progressively dry out. Under these conditions, groundwater, which contains little or no colloidal material, accounts for an increasingly larger fraction of streamflow than soil water. Because soil water appears to be the source of the stream colloids, stream colloid concentrations fall during summer baseflow conditions. The decline in stream colloid concentrations during summer baseflow conditions may reflect a decrease in macropore flow during drying periods because macropores would be expected to drain before the less mobile water contained in the soil matrix, and macropore flow facilitates colloid transport through the soil (DeNovio et al., 2004; Laegdsmand et al., 1999; Wang et al., 2014). Decreasing IS occurs when the watershed is becoming progressively wetter and soil water and macropore flow likely constitute a larger component of the streamflow. Mobilization of colloids that were generated through soil drying processes would occur during wetting periods and decreasing IS. These processes would not occur during soil drying and increasing IS and could explain the observed decrease in colloid concentrations during periods of increasing IS. The elevated colloid concentrations and generally low IS values observed during the winter and spring occur when wetter conditions prevail in the watershed and soil water is mobile.

Conclusion

Colloidal particle concentrations were measured in stream and groundwater samples collected over a 2-yr period with a wide range in hydrologic and chemical conditions, and concentrations were evaluated in the context of the changing hydrologic regime. Colloidal particles were dominated by Si, Fe, and Al and were present in nearly all stream samples but were not detected in groundwater samples. The inferred chemical composition, along with XRD and scanning electron microscopy analysis, indicated colloids were primarily composed of kaolinite and illite clays, with lesser amounts of amorphous Fe-hydroxides. Colloidal particles constituted between 32 and 36% of the Si flux and 93 to 97% of the Fe and Al flux in the <0.45- μm fraction in the stream. The colloid composition exhibited little variability over wide ranges in flow, but concentrations varied in response to changes in flow regime. Colloid concentrations were generally higher under high-flow conditions and were not detected during baseflow conditions when groundwater dominates streamflow, consistent with the absence of colloidal particles in groundwater samples. Colloid concentrations increased sharply during precipitation events that followed dry conditions in the watershed. Spikes in colloid concentration during the first infiltration events after soil drying have been observed in laboratory column experiments. Additionally, colloid concentrations tended to increase with decreasing stream IS due to increases in the repulsive forces predicted by DLVO theory between colloids and surfaces. Low stream water IS is observed during generally wetter conditions in the watershed when shallower flowpaths are active. Mechanisms of colloid mobilization that have also been observed in laboratory studies appear to explain the observations presented here at the watershed scale,

but changing hydrologic flowpaths also likely contribute to the observed patterns in streamwater colloid concentrations.

Acknowledgments

This work was supported by funding from the US National Science Foundation, Geoscience Directorate, Earth Science Division. The authors thank Nathan Rock and Clayton Jensen for their efforts in field and laboratory work. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government.

References

- Amo, Y.D., and M.A. Brzezinski. 1999. The chemical form of dissolved Si taken up by marine diatoms. *J. Phycol.* 35(6):1162–1170. doi:10.1046/j.1529-8817.1999.3561162.x
- Anderson, S.P., R.S. Anderson, and G.E. Tucker. 2012. Landscape scale linkages in critical zone evolution. *C. R. Geosci.* 344:586–596. doi:10.1016/j.crte.2012.10.008
- Anderson, S.P., E.L. Hinckley, P. Kelly, and A. Langston. 2014. Variation in critical zone processes and architecture across slope aspects. *Procedia Earth Planet. Sci.* 10:28–33. doi:10.1016/j.proeps.2014.08.006
- Andersson, K., R. Dahlqvist, D. Turner, B. Stolpe, T. Larsson, J. Ingri, and P. Andersson. 2006. Colloidal rare earth elements in a boreal river: Changing sources and distributions during the spring flood. *Geochim. Cosmochim. Acta* 70(13):3261–3274. doi:10.1016/j.gca.2006.04.021
- Befus, K.M., A.F. Sheehan, M. Leopold, S.P. Anderson, and R.S. Anderson. 2011. Seismic constraints on critical zone architecture, Boulder Creek Watershed, Front Range, Colorado. *Vadose Zone J.* 10(3):915–927. doi:10.2136/vzj2010.0108
- Bergendahl, J., and D. Grasso. 2000. Prediction of colloid detachment in a model porous media: Hydrodynamics. *Chem. Eng. Sci.* 55(9):1523–1532. doi:10.1016/S0009-2509(99)00422-4
- Beven, K., and P. Germann. 1982. Macropores and water flow in soils. *Water Resour. Res.* 18(5):1311–1325. doi:10.1029/WR018i005p01311
- Bradford, S.A., and S. Torkzaban. 2015. Determining parameters and mechanisms of colloid retention and release in porous media. *Langmuir* 31(44):12096–12105. doi:10.1021/acs.langmuir.5b03080
- Bradford, S.A., B. Headd, G. Arye, and J. Šimůnek. 2015. Transport of *E. coli* D21g with runoff water under different solution chemistry conditions and surface slopes. *J. Hydrol.* 525:760–768. doi:10.1016/j.jhydrol.2015.04.038
- Cheng, T., and J.E. Saiers. 2009. Mobilization and transport of in situ colloids during drainage and imbibition of partially saturated sediments. *Water Resour. Res.* 45(8). doi:10.1029/2008WR007494
- Corapcioglu, M.Y., and S.Y. Jiang. 1993. Colloid facilitated groundwater contaminant transport. *Water Resour. Res.* 29(7):2215–2226. doi:10.1029/93WR00404
- Dahlqvist, R., et al. 2007. Temporal variations of colloidal carrier phases and associated trace elements in a boreal river. *Geochim. Cosmochim. Acta* 71(22):5339–5354. doi:10.1016/j.gca.2007.09.016
- de Jonge, L.W., C. Kjaergaard, and P. Moldrup. 2004. Colloids and colloid-facilitated transport of contaminants in soils: An introduction. *Vadose Zone J.* 3(2):321–325.
- DeNovio, N.M., J.E. Saiers, and J.N. Ryan. 2004. Colloid movement in unsaturated porous media: Recent advances and future directions. *Vadose Zone J.* 3(2):338–351.
- Derjaguin, B., and L. Landau. 1941. Theory of the stability of strongly charged lyophobic soils and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim. URSS* 14:633–662.
- Dethier, D.P., P.W. Birkeland, and J.A. McCarthy. 2012. Using the accumulation of CBD-extractable iron and clay content to estimate soil age on stable surfaces and nearby slopes, Front Range, Colorado. *Geomorphology* 173:17–29. doi:10.1016/j.geomorph.2012.05.022
- Diek, S., A. Temme, and A. Teuling. 2014. The effect of spatial soil variation on the hydrology of a semi-arid Rocky Mountains catchment. *Geoderma* 235:236:113–126. doi:10.1016/j.geoderma.2014.06.028
- Freeman, L.A., M.C. Carpenter, D.O. Rosenberry, J.P. Rousseau, R. Unger, and J.S. McLean. 2004. Use of submersible pressure transducers in water-resources investigations. USGS, Reston, VA.
- Gable, D.J., 1996. Mineralogy, geochemistry, metamorphism, and provenance of the early Proterozoic metamorphic rocks of the central Front Range, Colorado. USGS, Reston, VA.
- Gran, G. 1952. Determination of the equivalence point in potentiometric titrations: Part II. *Analyst (Lond.)* 77(920):661–671. doi:10.1039/an9527700661

- Grolimund, D., and M. Borkovec. 1999. Long term release kinetics of colloidal particles from natural porous media. *Environ. Sci. Technol.* 33(22):4054–4060. doi:10.1021/es990194m
- Grout, H., M.R. Wiesner, and J.Y. Bottero. 1999. Analysis of colloidal phases in urban stormwater runoff. *Environ. Sci. Technol.* 33(6):831–839. doi:10.1021/es980195z
- Hiemenz, P.C., and R. Rajagopalan. 1997. Principles of colloid and surface chemistry, third edition, revised and expanded. CRC Press, Boca Raton, FL. doi:10.1201/9781315274287
- Hinckley, E.-L.S., et al. 2014. Aspect control of water movement on hillslopes near the rain-snow transition of the Colorado Front Range. *Hydrol. Processes* 28(1):74–85. doi:10.1002/hyp.9549
- Hunter, R.J. 1981. Zeta potential in colloid science. Academic Press, London, UK.
- Jarvie, H.P., et al. 2012. Role of riverine colloids in macronutrient and metal partitioning and transport, along an upland-lowland land-use continuum, under low-flow conditions. *Sci. Total Environ.* 434:171–185. doi:10.1016/j.scitotenv.2011.11.061
- Kanti Sen, T., and K.C. Khilar. 2006. Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. *Adv. Colloid Interface Sci.* 119(2-3):71–96. doi:10.1016/j.cis.2005.09.001
- Kaplan, D.I., P.M. Bertsch, D.C. Adriano, and W.P. Miller. 1993. Soil-borne mobile colloids as influenced by water flow and organic carbon. *Environ. Sci. Technol.* 27(6):1193–1200. doi:10.1021/es00043a021
- Khilar, K.C., R.N. Vaidya, and H.S. Fogler. 1990. Colloidally-induced fines release in porous media. *J. Petrol. Sci. Eng.* 4(3):213–221. doi:10.1016/0920-4105(90)90011-Q
- Kimball, B.A., E. Callender, and E.V. Axtmann. 1995. Effects of colloids on metal transport in a river receiving acid-mine drainage, Upper Arkansas River, Colorado, USA. *Appl. Geochem.* 10(3):285–306. doi:10.1016/0883-2927(95)00011-8
- Kretzschmar, R., M. Borkovec, D. Grolimund, and M. Elimelech. 1999. Mobile subsurface colloids and their role in contaminant transport. *Adv. Agron.* 66:121–193. doi:10.1016/S0065-2113(08)60427-7
- Kretzschmar, R., and T. Schafer. 2005. Metal retention and transport on colloidal particles in the environment. *Elements* 1(4):205–210. doi:10.2113/gselements.1.4.205
- Laegdsmand, M., K.G. Villholth, M. Ullum, and K.H. Jensen. 1999. Processes of colloid mobilization and transport in macroporous soil monoliths. *Geoderma* 93(1-2):33–59. doi:10.1016/S0016-7061(99)00041-5
- Leo, M.L., and S.P. Leen. 2013. Handbook of water analysis, 3rd ed. CRC Press, Boca Raton, FL.
- Majdalani, S., E. Michel, L. Di-Pietro, and R. Angulo-Jaramillo. 2008. Effects of wetting and drying cycles on in situ soil particle mobilization. *Eur. J. Soil Sci.* 59(2):147–155. doi:10.1111/j.1365-2389.2007.00964.x
- McCarthy, J.F., and L.D. McKay. 2004. Colloid transport in the subsurface: Past, present, and future challenges. *Vadose Zone J.* 3(2):326–337.
- McCarthy, J.F., and C. Degueldre. 1993. Sampling and characterization of colloids and particles in groundwater for studying their role in contaminant transport. *Environ. Particles* 2:247–315.
- McCarthy, J.F., and J.M. Zachara. 1989. Subsurface transport of contaminants—Mobile colloids in the subsurface environment may alter the transport of contaminants. *Environ. Sci. Technol.* 23(5):496–502.
- Mohanty, S.K., J.E. Saiers, and J.N. Ryan. 2015. Colloid mobilization in a fractured soil during dry-wet cycles: Role of drying duration and flow path permeability. *Environ. Sci. Technol.* 49(15):9100–9106. doi:10.1021/acs.est.5b00889
- Morrison, M., and G. Benoit. 2001. Filtration artifacts caused by overloading membrane filters. *Environ. Sci. Technol.* 35(18):3774–3779. doi:10.1021/es010670k
- National Atmospheric Deposition Program (NADP). 2015. NADP Program Office, Illinois State Water Survey. Univ. of Illinois, Champaign. <http://nadp.sws.uiuc.edu/data/> (accessed 6 Jan. 2015).
- National Resource Conservation Service (NRCS). 2016. <http://www.wcc.nrcs.usda.gov/basin.html> (accessed 10 Sept. 2016).
- Packman, A.I., N.H. Brooks, and J.J. Morgan. 2000. Kaolinite exchange between a stream and streambed: Laboratory experiments and validation of a colloid transport model. *Water Resour. Res.* 36(8):2363–2372. doi:10.1029/2000WR900058
- Pokrovsky, O.S., and J. Schott. 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chem. Geol.* 190(1-4):141–179. doi:10.1016/S0009-2541(02)00115-8
- Ragueneau, O., P. Tréguer, A. Leynaert, R.F. Anderson, M.A. Brzezinski, D.J. DeMaster, R.C. Dugdale, J. Dymond, G. Fischer, R. François, C. Heinze, E. Maier-Reimer, V. Martin-Jézéquel, D.M. Nelson, and B. Quéguiner. 2000. A review of the Si cycle in the modern ocean: Recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. *Global Planet. Change* 26(4):317–365. doi:10.1016/S0921-8181(00)00052-7
- Rantz, S.E. 1982. Measurement and computation of streamflow. USGS, Reston, VA. <https://pubs.usgs.gov/wsp/wsp2175/> (accessed 10 Nov. 2016).
- Rousseau, M., L. Di Pietro, R. Angulo-Jaramillo, D. Tessier, and B. Cabibel. 2004. Preferential transport of soil colloidal particles: Physicochemical effects on particle mobilization. *Vadose Zone J.* 3(1):247–261. doi:10.2136/vzj2004.2470
- Roy, S.B., and D.A. Dzombak. 1997. Chemical factors influencing colloid-facilitated transport of contaminants in porous media. *Environ. Sci. Technol.* 31(3):656–664. doi:10.1021/es9600643
- Ryan, J.N., and M. Elimelech. 1996. Colloid mobilization and transport in groundwater. *Colloids Surf. A Physicochem. Eng. Asp.* 107:1–56. doi:10.1016/0927-7757(95)03384-X
- Ryan, J.N., and P.M. Gschwend. 1994. Effects of ionic-strength and flow-rate on colloid release—relating kinetics to intersurface potential-energy. *J. Colloid Interface Sci.* 164(1):21–34. doi:10.1006/jcis.1994.1139
- Saiers, J.E., G.M. Hornberger, D.B. Gower, and J.S. Herman. 2003. The role of moving air-water interfaces in colloid mobilization within the vadose zone. *Geophys. Res. Lett.* 30(21). doi:10.1029/2003GL018418
- Torkzaban, S., S.M. Hassanizadeh, J.F. Schijven, and H.H.J.L. Van Den Berg. 2006. Role of airwater interfaces on retention of viruses under unsaturated conditions. *Water Resour. Res.* 42(12). doi:10.1029/2006WR004904
- Turner, B.L., M.A. Kay, and D.T. Westermann. 2004. Colloidal phosphorus in surface runoff and water extracts from semiarid soils of the western United States. *J. Environ. Qual.* 33(4):1464–1472. doi:10.2134/jeq2004.1464
- Wan, J., and J.L. Wilson. 1994. Colloid transport in unsaturated porous media. *Water Resour. Res.* 30(4):857–864. doi:10.1029/93WR03017
- Wang, Y., S.A. Bradford, and J. Šimůnek. 2014. Physicochemical factors influencing the preferential transport of in soils. *Vadose Zone J.* 13(1). doi:10.2136/vzj2013.07.0120