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Zeta potential of clay-size particles in urban rainfall–runoff during hydrologic transport

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Summary Urban rainfall–runoff transports a wide spectrum of anthropogenic aqueous complexes and particulate matter (PM). Zeta potential (ξ) as an electrostatic parameter provides an index of destabilization for clay-size particles (<2 μm) transported during hydrologic processes including passage of the runoff hydrograph. However, ξ of PM in urban rainfall–runoff has rarely been studied due to the dynamic and complex hydrologic, physical and chemical nature of rainfall–runoff systems. This study examined a series of rainfall–runoff events captured from a paved source area catchment in Baton Rouge, LA to characterize ξ of clay-size particles. The ξ of clay-size particles was also examined as a function of hydrologic transport with coupled water chemistry variables. Study results indicated that ξ varied from approximately −15 to −30 mV across the hydrograph of each event and generally mimicked the runoff intensity during hydrologic transport. Hydrologic transport results indicate while ξ was inversely correlated to the hydrograph flow rate, this inverse correlation was a function of variations in water chemistry parameters (pH and ionic strength); parameters that were driven by hydrologic flow rate. For each event ξ exhibited hysteretic trends as a function of rainfall–runoff ionic strength and pH during the passage of the hydrograph. Results demonstrate that hydrologic transport played an important role driving both water chemistry and ξ trends for clay-size particles; as well as treatment behavior of rainfall–runoff unit operations and processes.

Introduction

Urban rainfall–runoff transports a very wide gradation of PM, from smaller than 1 μm (colloidal-size) to greater than 10,000 μm (gravel-size), generated from anthropogenic and biogenic activities, pavement, tire interaction, and vehicular part abrasion (Muschack, 1990; Sansalone et al., 1998).

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Nomenclature

AADT	average annual daily traffic (vehicles/day)
EC	electrical conductivity (μS/cm)
I	ionic strength (mol/L)
$N_{2\text{-}\mu m}$	number density for clay-size particles (<2 μm) (#/L)
N_T	number density for total particles (<250 μm) (#/L)
PND	particle number density (#/mL)
PSD	particle size distribution
t_{max}	duration of runoff (min)
TSS	total suspended solid (mg/L)
VPV	vehicle per runoff volume (vehicles/L)
V_t	total runoff volume throughout the event (L)
ξ	zeta potential (mV)

Based on the United States Department of Agriculture (USDA) classification scheme clay particle sizes are classified as particles nominally less than 2 μm in size (Coduto, 1999; Soil Survey Division Staff, 1993). Larger PM classes such as gravel, sand and to a lesser degree coarse silt-size (<75 μm) PM are commonly removed from runoff through sedimentation unit operations or possibly separated to varying degrees in the upstream drainage system. However, colloids (<1 μm), suspended PM including clay-size, and the finer fractions of silt-size classes of PM are more likely to remain entrained in runoff and discharged to receiving waters.

Past studies have identified that while the colloidal and clay-size (<2 μm) fractions of particles may constitute a small gravimetric percentage of the gradation on a mass basis, these entrained particles can be of significant importance with respect to transport and bioavailability of metals and organic compounds (Forstner et al., 2001; Wells and Goldberg, 1991, 1993; Yuan et al., 2001). In the aqueous environment, clay particles are surface active and react with metal species and organics due to high specific surface area. Their reactions with different components in natural waters are also rapid (Langmuir, 1997). By definition, higher concentrations of metals and organics mass, when normalized to particulate mass, have a greater association with the clay-size fraction of the particle gradation (Celis et al., 2000; Gibbs, 1973; Schroth and Sposito, 1998). In addition, fine silt and clay-size particles are the major contributor to turbidity as compared to settleable (<75 μm) and sediment-size (>75 μm) particles in overall particle size distribution (PSD) (Gippel, 1995). Such turbidity can result in deleterious impacts to aquatic plants sensitive to light availability (Poole and Bowles, 1999). These colloidal and clay-size fractions (<2 μm) of the gradation are also more challenging to treat by primary physical unit operations (Gromaire-Mertz et al., 1999) which utilize mechanisms based on particle gravimetric attributes such as size and density. For the control of colloidal and clay-size particles, these attributes and mechanisms are of lesser importance in comparison to electrostatic indices (Sansalone and Kim, 2008) particle number density (PND) indices (Cristina et al., 2002) and variations of such indices and water chemistry under common transport and treatment conditions.

Zeta potential (ξ) is an important electrostatic parameter for particles suspended in an aqueous medium as an index measurement when evaluating the stability of suspended dispersions with respect to particle aggregation and understanding the performance of physical operations such as flocculation, flotation and sedimentation of such suspensions (Elimelech et al., 2006; Hunter, 1981). ξ has been used in drinking/wastewater treatment for routine process and quality control measurements (Darby and Lawler, 1990; Sharp et al., 2005) or for research and development at an array of various industries, such as pharmaceuticals (Mahato et al., 1995), paper making (Van de Ven, 1999), biomedicine (Riddick, 1968), and paints (Fujitani, 1996).

The net surface charge, expressed as ξ of most particles in surface water at neutral pH is negative and in the range of -15 to -30 mV (Ongerth and Pecoraro, 1996). ξ of wastewater particles has also been studied (Elmitwalli et al., 2001) and the mean ξ for raw sewage was reported as -22.6 mV. The reduction or depression of this negative charge, as for example through metal salt coagulation, is utilized to provide particle destabilization in a wide variety of water treatment unit operations and processes (UOPs).

A number of chemical and physical parameters influence ξ (or electrophoretic mobility) of PM with a homogeneous mineralogy. The chemical parameters include concentration of solute additions, for example a metal salt, solution ionic strength, pH, and electrolyte type (i.e. NaCl, $NaNO_3$ and KCl) (Ntalikwa et al., 2001). The parameters include PM conductance/shape, properties of various particles, distribution of electrolyte ions in the double layer, and temperature and viscosity of the solution. Among these various parameters, this study focused on pH and ionic strength. Many studies have examined the impact of pH on ξ of specific inorganic oxides (Fe_2O_3) (Wnek and Davies, 1977), (TiO_2) (Rastogi and Srivasta, 1973), and (Al_2O_3) (Elimelech et al., 2006). For these oxides lower pH resulted in ξ trending towards a more positive direction, with the reverse trend occurring for higher pH. Many researchers and scientists have conducted a series of experiments to test influence of ionic strength on ξ of various particles or membranes under different types and concentrations of electrolytes (Fievet et al., 2001; Hosse and Wilkinson, 2001; Hsu and Huang, 2002). One of the common findings from these studies is that in general the increase of ionic strength in solution pushes ξ toward more positive values, although the wide ranges of variations were found depending on type and concentration of electrolytes.

Compared to wastewater and natural water, quantity and quality control of urban rainfall–runoff continues to pose unique and difficult challenges due to the highly unsteady and stochastic nature of hydrologic transports and interacting processes between traffic-generated and dry deposition particles and rainfall–runoff. For example, variations in flow and concentration can exceed an order of magnitude during a single rainfall event and between events. Partitioning and speciation kinetics are generally