Influence of pH on Organic and Inorganic Colloids in Stormwater

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ABSTRACT
Urban runoff usually contains significant amounts of organic and inorganic colloidal particles. Due to their high surface area and associated surface charges, these colloidal particles become a strong binding site and carriers for many contaminants found in the runoff. This paper presents a study on the physicochemical properties and behaviors of organic colloidal particles found in urban runoff under different simulated pH conditions. Four optical characterization techniques, namely (1) UV spectroscopy; (2) fluorescence spectroscopy; (3) size-exclusion chromatography with UV detector and (4) dynamic light scattering were used to examine and evaluate the colloidal properties and their behaviors. It was found that the colloidal particles under both acidic and alkaline conditions exhibited a distinct bimodal characteristic in particle-size distribution. Parallel interpretation of the four optical characterization results revealed that the influence of pH on the colloidal particles were more prominent at alkaline conditions, where an enormous growth of larger colloidal particles was observed as a result of aggregation and/or dissolution of humics and fulvic-type substances as well as biopolymers and their precursors. Results showed that the colloidal particles behave differently under acidic, neutral and alkaline conditions. This has an important implication on the water quality and immediate water treatment processes are required.

Keywords: contaminant transport, humic type substances, organic colloidal particles, urban runoff

INTRODUCTION
Urban runoff usually contains a wide range of chemical and biological contaminants. These contaminants include organics (e.g. oil, grease, humic substances, hydrocarbons), inorganics (e.g. metals, silica and nutrients) and pathogens, which often cause severe water quality problem that results in detrimental impacts on ecology and biodiversity of the receiving water bodies (Schiff et al. 2003; Walsh 2004). The contaminants are usually present in either solid, colloidal or dissolved phases. The partition of contaminants among these phases depends on various environmental factors, and one of the most prominent factors is the pH condition. The degree to which the contaminants in stormwater are being partitioned to particles, colloidal and dissolved states has an important implication for their transport in receiving water bodies, as well as their bioavailability and inherent biological effects.

Among the partitioned phases, colloidal phase has been considered as the most important area in contaminant transport because of its high surface area and associated surface charge. In general, colloids are defined as particles with sizes ranging from 1 to 1,000 nm. Organic colloids in stormwater are chemically heterogeneous mixture of many macro and micro molecules (humic and fulvic, phenolic-type substances) that are rich in acidic and basic functional groups. They are the major binding substrates for
contaminant transport because of their associated surface charges. He and Wang (2011) observed the adsorption of polycyclic aromatic hydrocarbons (PAHs) on humic-type substances. They observed that the aromatic properties of humic-type substances are the main underlying factors to transport PAH; where they are interacted via $\pi-\pi$ electron transfer mechanism. Sharma et al. (1985) found that the transport of bacteria in sandpacks increased when their negative surface charge also increased. Fletcher and Loeb (1979) found that positively charged surface attracted more bacteria than negatively charged surface. Vasil’eva et al. (2009) reported that the presence of fulvic type substances may enhance the transport of some toxic metals more than 10 times by natural biologically active substances.

As most of the contaminants in urban runoff are bound to colloidal particles, the bioavailability and inherent biological effects are likely to be strongly affected by the pH conditions. While the particle-bound contaminants and their transport within the urban environment are reasonably well understood (Aryal et al., 2006; Kang et al., 2007; Badin et al., 2008), there has been limited understanding of colloidal particles in stormwater and the environmental influence of pH conditions on them (Grout et al., 1999; Zgheib et al., 2011). The stormwater pH range of 6 to 8 is common (Mohammed et al., 2011) but literature has reported pH values of less than 4.5 and also higher than 8.5 (Gupta et al., 1981). The existing stormwater literatures focus mostly on the particle-bound or dissolved phases of heavy metals, organics, pathogens or nutrients. Considering the limited available information on the colloidal particles in stormwater, this study aims at evaluating the physicochemical characteristics and behaviors of organic colloidal particles, which is one of the major concerns in water treatment/management, at different simulated environmental pH conditions. This knowledge will lead to the understanding of contaminant partition under different pH conditions which in turn, will enable the water treatment operators to optimize the removal efficiency in water treatment processes such as coagulation, filtration, ultraviolet disinfection and others.

MATERIALS AND METHODS
Stormwater samples were collected from urban drains at four different locations in South East Queensland during rainfall events. The four locations covered medium density residential area (S1), low density residential area (S2), street runoff (S3) and green park runoff (S4). All the stormwater samples were collected in polypropylene tubes that were pre-washed with nitric acid (Univar Australia) and milliQ water using a grab sampling method at the inlet of stormwater drainage. Three samples were grabbed at an interval of 10 minutes and mixed to represent the stormwater. The samples were filtered through 1.2 $\mu$m glass fibre filters (GF/C Whatman, USA). The pH of the solution was adjusted by adding hydrochloric acid (Univar Australia) or sodium hydroxide (NaOH) into the filtrate to achieve the respective simulated pH levels (pH 3, 5, 7, 9 and 11) to represent extreme lower pH as well as higher pH in stormwater. Each pH-adjusted solution was analysed using four different optical spectroscopy characterization methods: (1) ultraviolet (UV) spectroscopy, (2) fluorescence spectroscopy (i.e. excitation emission matrix, EEM), (3) gel permeation chromatography equipped with UV detector and (4) dynamic light scattering (DLS) particle size analysis.
UV Analysis
The stormwater samples adjusted to various pH levels were analysed using UV spectrometer (Varian 50 Bio, Varian, USA). The instrument was operated at bandwidth 1 nm, with quartz cell of 10 mm path length, wavelength of 190 to 400 nm and at a scanning speed of 190 nm/min (slow). In this instance, the photometric accuracy was 0.004 Abs at 1.0 Abs.

Fluorescence Analysis
Three-dimensional fluorescence spectra (EEM) were obtained using a spectrofluorometer (Perkin Elmer LS 55, Perkin Elmer, USA) with a wavelength range of 200 nm to 500 nm (for excitation); and 280 nm to 500 nm (for emission). The spectra were taken at an incremental wavelength of 5 nm in excitation (Ex); and 2 nm in emission (Em). The EEM value of blank (Milli-Q water) data was subtracted from the analyzed samples for blank correction. The data obtained from EEM was analyzed using Microsoft Excel.

Size-Exclusion Chromatographic Analysis
Size-exclusion analysis was carried out using HP-SEC (Shimadzu, Japan) that consisted of a column (TSK Gel G3000SWxl, Tosoh, Japan) with UV detector (SPD M20A, Shimadzu, Japan). A flow rate of 1.0 mL/min was used for the elution of 0.3 M sodium chloride (Univar Australia) in 0.05M phosphate buffer solution. The sample injection volume used was 100 µL.

Particle-Size Distribution Analysis
Particle-size distribution was measured by dynamic light scattering (DLS) method using Zetasizer NanoZS (Malvern, UK). The instrument has an option to measure specific colloids if refractive index is known. Humic-type substances were selectively measured by selecting its refractive index 1.33 during analysis to represent organic colloids.

RESULTS AND DISCUSSION
The organic contents in stormwater samples were measured using a total organic carbon analyzer (Analytik Jena multi N/C 3100, AnalytikJena, UK) prior to optical analysis. The organic content was found highest in S4 (5.5 mg/L) followed by S2 (4.9 mg/L), S1 (3.7 mg/L) and S3 (2.3 mg/L). The results show that organic concentration in the samples was influenced by green coverage.

UV Analysis
Ultraviolet absorption spectra (190 - 400 nm) provide information on the nature and quantity of substances, change in the functional group composition and alteration in colloidal particles (Korshin et al., 1997; Aryal et al., 2011). Fardad and Massudi (2007) applied UV spectroscopy to understand the pH effect on metal oxide nanoparticles. They observed similar spectra for analogous particles but a shift towards larger wavelength was evident at higher pH values.

Figure 1 shows the UV absorbance of colloidal particles in stormwater samples collected at four sites (S1 - S4) at pH 3, 7 and 11. All four samples had similar UV spectral intensity, as well as their trend under both acidic and neutral pH conditions. Under alkaline condition, the spectral intensity was almost two times higher at the lower
wavelength range (190 - 205 nm). This result shows that colloidal particles behave differently to a greater extent under alkaline conditions than the acidic condition. It is believed that organic colloids (macromolecules with acidic functional groups) started to dissolve under alkaline conditions that increased the spectral intensity (Plaschke et al., 1999).

Fluorescence Analysis
Fluorescent spectroscopy is one of the most promising analytical tools to identify the nature of organics based on their properties. Fluorescence spectra is also known as excitation emission matrix (EEM), and has been widely used to identify the nature of organic substances found in water, stormwater and wastewater (Chen et al., 2003; Sheng and Yu, 2006; Aryal et al., 2009).

Figure 2 shows the fluorescence spectra of samples collected at four sites (S1 - S4) under different simulated pH conditions. The spectra (Ex : Em 200 - 500 nm : 280 - 500 nm) showed a significant pH influence on the fluorescence intensity for colloid particles. Among the three spectra, pH 3 spectra exhibited peak at a lower excitation and emission region (Ex 200 - 250 nm and Em 280 - 330 nm). At neutral pH, the spectral characteristics are similar, but the peak intensities are lower than the spectra at pH 3. However, at alkaline pH, the peak intensity area was found to widen at higher Ex and Em regions (Ex 200 - 500 nm : Em 330 - 500 nm). When the fluorescence intensity of sample at neutral pH was made as the reference point, the lower pH samples (i.e. pH 3 and 5) were found to have 2.5 times higher intensity peak whereas the higher pH samples (i.e. pH 9 and 11) had only half of the peak intensity at Ex : Em region 200 -
280 nm : 280 - 380 nm (e.g. amino acids, peptides and biopolymers). At the Ex : Em region of 280 - 500 nm : 380 - 500 nm (e.g. fulvic and humic-type substances), samples at lower and higher pH had 1.5 - 1.8 and 8 - 10 times higher intensity, respectively. This result implies that the increase in UV absorbance is associated with the increase of pH.

Under acidic pH conditions, the peak appeared at lower wavelength, which is possibly due to: (1) the dissolution of amphoteric proteins and their precursors and/or fulvic type
substances (Aryal et al., 2009; Saab et al., 2010) and (2) the possible aggregation of humic-type substances (Plaschke et al., 1999). The first assumption is supported by the presence of peak at Ex : Em 250 : 320 nm which primarily reflects biopolymers peak. The aggregation of humic-type substances is supported by the shifting of the EEM spectra. At alkaline pH on the other hand, deprotonation of proteins and its precursors, as well as the humic-type substances may start resulting to the solubilization of organics. This may have caused a broader spectrum of organics in the EEM spectra.

Size-Exclusion Analysis

Size-exclusion chromatography is a technique used to understand the particle sizes of organics and inorganics present within the samples. In this method, the colloidal particles in solution are separated according to their sizes.

Figure 3 shows the size distribution of colloidal particles in samples collected at four sites (S1 - S4) at pH 3, 7 and 11. The rigid vertical line represents the colloidal size present in the peak region. At neutral pH, the peak intensity and width were narrow. At acidic pH, the ratio of smaller to larger particles was low and this ratio increased with pH. This is because most of the inorganic colloids and fulvic-type substances are dissociated and/or dissolved at acidic pH while many inorganics such as metal ions are precipitated and some organics of high molecular weight such as humic and biopolymer-type substances are dissolved at higher pH. Precipitation of metal ions and dissolution of humic and biopolymer-type substances may increase the volume/number of colloids. Broader and intense peaks around 5 to 9 minutes in alkaline pH provide justification for this observation. In this instance, the earlier peaks at 5.5 min are biopolymers whereas later peaks around 8 min are humic and fulvic-type substances.

![Fig. 3 - Size distribution of colloidal particles in sample collected at four sites (S1 - S4) at pH 3, 7 and 11 and UV wavelengths of 210 and 228 nm.](image-url)
Dynamic Light Scattering Analysis

Dynamic light scattering (DLS) is a technique used to measure the Brownian motion (diffusion) of the particle and its subsequent size distribution (number) within the solution. In this instance, the DLS was used to study the organic colloidal behavior in stormwater. Figure 4 shows the size distribution of particles by volume (%) in samples collected at four sites (S1 - S4) at pH 3, 7 and 11.

At neutral pH, the distribution exhibited a unimodal characteristic (50 - 200 nm) showing the continuum in particle sizes within the sample ranging from 50 - 500 nm where it ranged from 50 - 150 nm for samples at site S1, S2, and S4 and from 200 - 400 nm for site S3. Similar particle size result has been obtained by Plaschke et al., (1999) wherein the colloidal particles ranged from 40 - 110 nm under neutral pH. According to Plaschke et al. (1999), under neutral pH condition, humic-type substances may exert a rigid structure and form size in that range. This finding is similar to the observations for site S1, S2 and S4 where organic matter contribution was high. However, site S3 (impervious area) did not follow similar pattern. The reason for this difference is may be due to the contribution of other colloidal materials in stormwater generated by vehicular corrosion/abrasion in site S3.

Both acidic and alkaline pH shifted the particle size distribution from unimodal to bimodal distribution and the particle size range is also changed. These results suggested that the hydrodynamic size of organic colloidal substances largely depend on pH. Under acidic conditions, particle size appeared in the range of 20 - 30 nm and 200 - 400 nm.

Fig. 4 - Particle size distribution of humic-type substances in samples collected at sites S1 - S4 at pH 3, 7 and 11.
Appearance of smaller particle sizes implies the dissolution of fulvic-type substances and biopolymers. Larger particles that appeared in 200 - 400 nm sizes imply the possible aggregation of humic-type substances with the increase of pH (Plaschke et al., 1999). Some discrepancies occurred between the SEC and PSD results. For example, the authors observed a good peak for sample collected at site S1 at pH 3 in sizes of 20 - 40 nm in PSD. However, such a peak was not observed in SEC. This is possibly because the particles that appeared in PSD between 20 - 40 nm sizes are relatively less UV active substances. However, the overall result shows consistency in data obtained using the two analytical methods (SEC and PSD). Under alkaline conditions (pH 11), peaks appeared in between 20 - 40 nm and 60 - 400 nm sizes. The peaks indicate that there is dissolution of large macro molecules (humic and fulvic-type substances) that ranged in between 20 - 110 nm sizes and other unknown organics at alkaline pH.

Finally, the overall result reflects that neutral pH usually agglomerates/precipitates organic substances that result in the increase of colloids and their sizes. With the change in pH, organic matter may change the concentrations of species (humic, fulvic or phenolic-type substances) in stormwater to higher levels than expected from their thermodynamic solubility. This may enhance the transportation of contaminants much more than expected due to active charges on humic and fulvic-type substances.

CONCLUSIONS
The influences of pH on colloidal particles found in stormwater was studied by analyzing the colloidal samples (< 1.2 µm) using four different optical characterization methods.

- UV spectra showed differences in absorbance intensity at different pH conditions. The differences in absorbance intensity were identified to be owing to the shift in colloidal particle sizes at higher pH in stormwater.
- The fluorescence spectra showed a significant influence of pH on the fluorescence intensity of colloids, as well as the location of the peak. Almost 2.5 folds higher intensity was found at lower Ex : Em region for lower pH (pH 3) while, nearly half of the intensity at higher pH (pH 11). It was also observed that almost 1.5 - 1.8 and 8 - 10 times higher intensity at higher pH with respect to fluorescence at neutral pH (pH 7), which indicates that both acidic and alkaline environments significantly influence the physicochemical properties and behaviors of colloidal particles.
- Size-exclusion chromatography shows an enormous growth of smaller colloidal particles at lower pH condition, indicating the aggregation and/or dissolution of humic and fulvic type substances as well as biopolymers and their precursors.
- Particle-size distribution analysis showed bimodal distribution of colloidal particles at acidic and alkaline conditions, whereas continuum unimodal distribution characteristic was observed at neutral pH. The result reflected the presence of different types of contaminants in stormwater which might have drawn an electrostatic attraction charge towards the colloidal particles at different pH conditions.
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