Analysis of Colloidal Phases in Urban Stormwater Runoff

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The composition and morphology of colloidal materials entering an urban waterway (Brays Bayou, Houston, U.S.A.) during a storm event was investigated. Analyses of organic carbon, Si, Al, Fe, Cr, Cu, Mn, Zn, Ca, Mg, and Ba were performed on the fraction of materials passing through a 0.45 μm filter. This fraction, traditionally defined as "dissolved", was further fractionated by ultracentrifugation into colloidal and dissolved fractions. Colloids, operationally defined by this procedure, accounted for 17% of the carbon, 32% of the silica, 79% of the Al, 85% of the Fe, 52% of the Cr, 43% of the Mn, and 29% of the Zn present in filtrates when averaged over the storm event. However, the composition of colloidal material was observed to change over time. For example, colloids were predominantly composed of silica during periods of dry weather flow and at the maximum of the stormwater flow, while carbon dominated the colloidal fraction at the beginning and declining stages of the storm event. These changes in colloidal composition were accompanied by changes in colloidal morphologies, varying from organic aggregates to diffuse gel-like structures rich in Si, Al, and Fe. The colloidal phase largely determined the variability of elements in the 0.45 μm filtrate.

Introduction

By convention, filtration using a 0.45 μm membrane is typically used to define "dissolved" and "particulate" fractions of materials in water. However, it is widely recognized that this operationally defined "dissolved" fraction typically includes colloidal particles. Organic or inorganic compounds may be present as or associated with colloidal solid phases in a continuous spectrum of size down to the nanometer scale (*1*). Thus, colloids must be accounted for in describing phenomena such as chemical partitioning between phases, mobilization and transport of metals and organic contaminants, and the bioavailability of chemical species.

However, the characteristics of colloidal particles in natural waters are relatively unknown. Studies of sea, lake, and groundwaters (*2−7*) suggest that although colloidal (<1 μm) and fine particle fractions (1−60 μm) may account for

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a small amount of the total mass of suspended matter and mass deposited in sediments, they appear to be extremely important with respect to the transport and fate of metals and organic compounds. Numerous investigators have noted the potential influence of colloidal particles on the "apparent" solubility and partition coefficients for organic compounds (*8−10*). Approaches to correcting for the influence of colloidal material on contaminant partitioning have often considered colloids as a uniform phase. Nonetheless, very little is actually known about the composition or variability of colloidal materials in waters. To our knowledge only Nomizu et al. (*11−12*), Perret et al. (*13*), and Grout and Parron (*14*) have reported both morphological and chemical characterizations of colloidal matter in river waters. These studies considered colloidal characteristics in grab samples representing a single hydrological condition.

Recent work (*15, 16*) has highlighted the importance of fine particles and colloids in the transport of contaminants from urban watersheds during storm events and the variability of mass loadings over time. Colloidal contaminants may aggregate and make their way into sediments of receiving waters. The colloidal and fine particle fractions of suspended material may have a disproportionate influence on sediment and water qualities due to their high surface energy, mobility, and bioavailability. In addition, colloidal and fine particles are likely to be the key fraction of suspended particle mass contribution to light scattering. Thus, negative impacts on sensitive rooted aquatic plants arising from dredging and reduced light availability are likely to be linked to smaller size fractions of particles. In summary, the structure, composition, size, activity, and behavior of aquatic colloids is likely to play an important role in determining the quality of aquatic ecosystems, and the transport and fate of elements.

In this work, we describe the variety in composition, structure, and size of colloidal materials in an urban waterway during a storm event and how these characteristics changes over the duration of the runoff event. Evidence for the role of colloidal materials in influencing variability of water quality over time is presented.

Methods and Sampling

One storm event was monitored over a 24 h period from the beginning of the first rainfall in an urban waterway, Brays Bayou, located within the Houston metropolitan area (TX, USA). The portion of the Brays Bayou watershed sampled represents a drainage area of approximately 240 km² (*17*). During dry weather flow (approximately 2.8 m³/s) the Bayou has a depth of less than 1 m. During storm events, flow may increase to over 800 m³/s with a depth of over 8 m. The majority of the watershed is under stress from a variety of urban land uses, consisting mostly of residential and commercial properties. The soils drained are typical Uderts vertisols mainly composed of smectites (*18*). Brays Bayou was sampled at Main Street (Figure 1). At this location, Brays Bayou is a concrete channel which begins upstream at Gessner street. It carries a background flow of approximately 10 000 m³/h, as estimated from a USGS gaging station at Main street (*15*) with large increases in flow during storms. The storm event (June 25th, 1996) was preceded by a 2-month period without significant rainfall, during which time background conditions were sampled.

Samples were obtained by dropping a 11.5-L, detergent-cleaned, acid-rinsed, polyethylene bucket into the center of the runoff stream from overpasses spanning the Bayou. The bucket was rinsed with one volume of sample water, which was discarded, and then refilled with sample water. Once
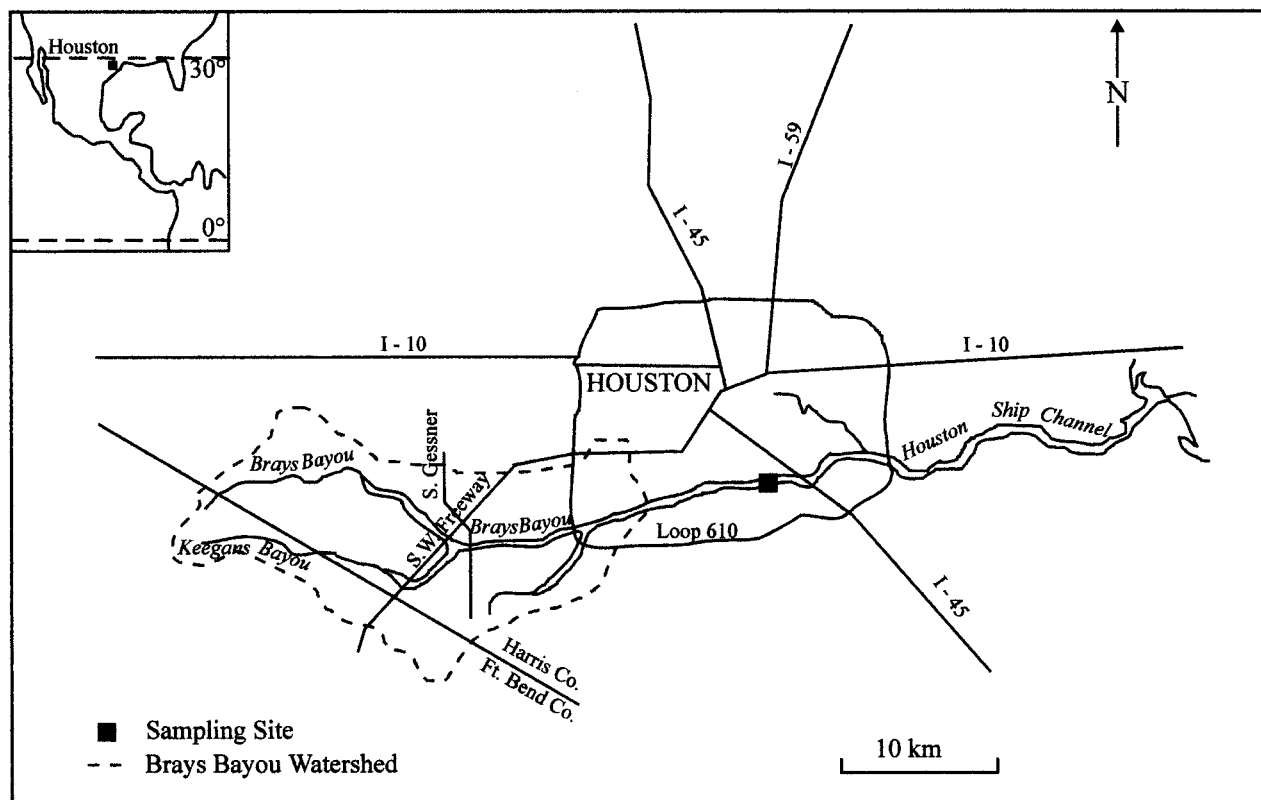
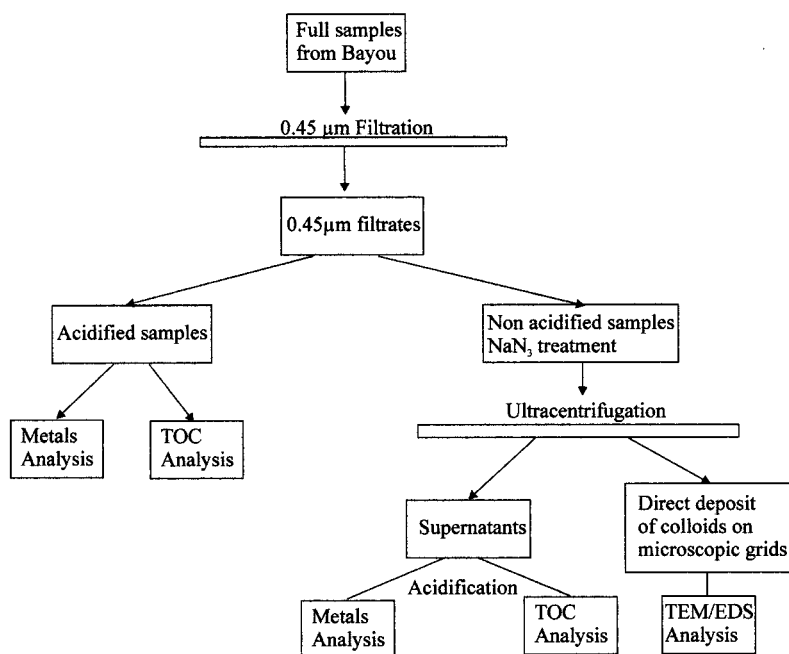FIGURE 1. Brays Bayou watershed and sampling site.

FIGURE 2. Sampling and analysis strategy.

the sample was retrieved, 1 L of runoff was poured into two 500 mL polyethylene bottles. Each bottle had been washed with Alconox cleaner, rinsed three times with distilled water, rinsed with a 10% HCl solution, and then given three final rinses with ultrapure water from a Millipore purification unit. The combined colloidal and dissolved fractions as conventionally defined were separated from the particulate fraction by filtration on a 0.45 μm membrane. Although widely applied in water analysis, this separation method cannot be considered as quantitative for colloids. The filtration system consisted of four 250 mL vacuum filter holders (Nalgene,

prod. 315-0047) mounted on 1000 mL Erlenmeyer flasks, each flask being connected to a vacuum pump (Gast, No 1HAB25 BM100X). The 0.45 μm membrane used in the filtration procedure was a cellulose nitrate membrane (Sartorius AG, Goettingen, Germany) 47 mm in diameter. Prior to use, each membrane was washed with a 10% HCl solution, rinsed with ultrapure water, and then dried at 37 °C. In each case, half (approximately 500 mL) of the filtrate was acidified to pH 1−2 with HNO_3 (EM Science, 69−71 wt %) for further analysis (Figure 2). Sodium azide (1 mg/L) was added to the remaining half of the filtrate to inhibit biological activity. All samples
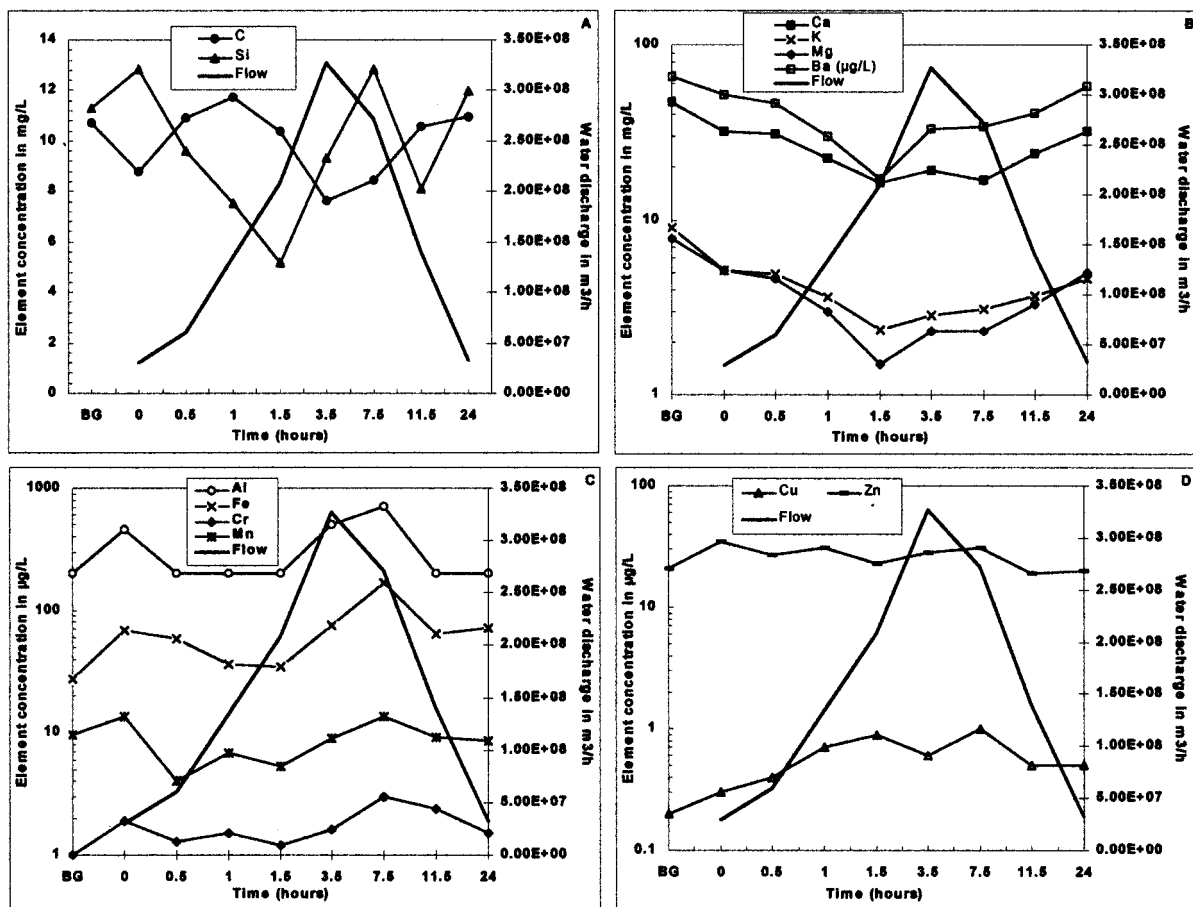
FIGURE 3. Element concentrations of the <0.45 μm fraction and water discharge throughout a storm event: (A) Si and C; (B) Ca, Mg, K, and Ba; (C) Al and Fe; and (D) Cr, Cu, Mn, and Zn (BG = background conditions, standard deviations to the mean are shown on Figure 4).

were placed in a refrigerator at approximately 4 °C until analysis. The nonacidified filtrates were centrifuged using a horizontal ultracentrifugation (30 000 rpm, 127 000g during 16 h at 10 °C). The supernatant, supposed to contain the "true" dissolved fraction, was carefully pipetted, into previously cleaned Nalgene bottles and acidified (HNO$_3$ to reach a pH between 1 and 2) prior to analyses. In parallel, also from the nonacidified filtrates, colloidal phases were directly deposited on Cu 200 mesh microgrids (previously coated by a collodion and carbon films and then by a protective Nanoplast resin film) following previously developed methods (13, 19, 14) by ultracentrifugation. Samples were typically filtered within 24 h of the storm event and in no case longer than 48 h. Total processing time between sampling, filtration, and ultracentrifugation was within 15 days.

The colloidal particles were characterized by coupling transmission electron microscopy (TEM, JEOL JEM 2000FX operating at 100 kV) observations with elemental chemical analysis using an energy dispersive spectrometer and analysis system for X-rays (Oxford/Link). The EDS data expressed in number of counts were recalculated in percent.

The filtrates and the supernatants obtained after ultracentrifugation were analyzed for Si, Al, Ba, and Mn by plasma emission spectroscopy using inductively coupled plasma (ICP-AES). Atomic absorption spectroscopy (AAS) in oven mode was used to measure Fe, Cr, and Cu and in flame mode for Mg, Ca, K, and Zn. Total organic carbon was measured using a TOC analyzer (TOC 500, Shimadzu). Analyses of each element for each filtrate and supernatant were repeated three times. Coefficients of variation were within 5% or less for C, Si, Ca, Mg, and Ba (when concentrations are >20 ng/L), no

more than 10% for Al, Fe, K, Mn, Zn, and Ba (when concentrations are <20 ng/L), and within 15% for Cr and 20% for Cu.

Results and Discussion

Chemical Composition of the Waters during a Storm Event. The concentrations of organic carbon, the elements Si, Ca, K, and Mg, and the individual metals (Al, Fe, Cr, Cu, Mn, Ba, and Zn) in the filtrates are plotted in Figure 3A–D. The average concentrations of Ba, Cr, Cu, Mn, and Zn observed over this storm event are very similar to those reported for other storm events we have observed in Brays Bayou (Table 1). However, relative to previously studied storms, the concentrations of C and Fe were slightly higher in the storm sampled for the current study. These higher concentrations may be related to the very long dry period antecedent to the storm event, although the cause of a differential impact of this factor on C and Fe is not clear.

Comparison of the average concentrations over the storm event to world averages estimated from the largest rivers in terms of water discharge and suspended matter load by Martin and Meybeck (21) shows also that the Brays Bayou runoff displays a chemical signature that, despite considerable anthropogenic influence, is quite similar to that of rivers with relatively undisturbed watersheds.

A detailed elemental analysis of concentrations over time in Brays Bayou reveals a group of the major elements Ca, Mg, and K and the trace element Ba that follow similar trends of decreasing concentration with increasing flow (Figure 3B). A second group comprised of the elements Si (Figure 3A), Al, Fe, Mn, and Cr (Figure 3C) exhibits two peak concentra-

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TABLE 1. Comparison of Average Element Concentrations throughout Different Storm Events[a]

av on storm data	April 1993 [1][b]	May 1993 [1][b]	Aug 1993 [1][c]	May 1994 [2][c]	June 1994 [2][c]	June 1996 [3][c]	world av [4]
C (mg/L)	7.5		7.47 (±1.95)	5.96 (±1.59)	4.95 (±0.95)	9.93 (±1.45)	6
Fe (µg/L)	92	53	72.33 (±43.21)	37.50 (±28.92)	22.44 (±6.47)	72.54 (±42.10)	40
Ba (µg/L)	31	32	42.83 (±15.56)	33.57 (±10.96)	19.50 (±7.12)	38.88 (±13.14)	60
Cr (µg/L)	0	0	6.63 (±4.93)	0.68 (±0.12)	0	1.80 (±0.61)	1
Cu (µg/L)	5	0	5.17 (±4.22)	2.79 (±0.49)	2.13 (±2.03)	0.61 (±0.24)	10
Mn (µg/L)	12	7	0.5 (±1.22)	6.93 (±5.22)	5.75 (±4.13)	8.75 (±3.51)	8.2
Zn (µg/L)	37	11	149.83 (±44.02)	65.57 (±46.20)	26.56 (±19.83)	26.75 (±5.68)	30

[a] Data from [1] Characklis, 1994, [2] Brejchova, 1996, [3] this study, and [4] Martin and Meybeck, 1979. [b] Storm (one data). [c] Average (n = 6) over storm progression.

tions: the first one occurring during the first few minutes of the storm event, and the second one immediately after the peak flow (t = 7.5 h). The elements Zn and Cu (Figure 3D) cannot be easily included in either of these two groups. Also, organic carbon (Figure 3A) follows a different trend, with peaks in concentration occurring early in the storm (t = 1 h) and then again as the flow returned to near dry-weather values (t = 11.5 h).

Decreasing concentrations of the elements Ba, Ca, K, and Mg with increasing flow suggests dilution as the storm progresses. The contrasting behavior of the elements Si, Al, Fe, Mn, Cr, Zn, and that of C appears to be more complex and could be linked to the relative concentrations of the dissolved and colloidal fractions during the storm.

Evidence and Quantification of the Colloidal Matter in Filtrates. The quantity of colloidal matter in the filtrates was calculated by taking the difference in concentration of individual elements before (dark circles on Figure 4) and after ultracentrifugation (white circles on Figure 4). A positive difference, expressed in percentage, represents the loss of a given element after centrifugation and, as a consequence, the percentage of this element in a colloidal phase. Taking into account the standard deviation of the three replicates for the same analysis, the colloidal material was considered significant if the loss by centrifugation was greater than 20% (histograms with a plain border). If the loss was less than or equal to 20%, the colloidal material was considered insignificant (histograms with a dotted border). Negative losses are not feasible (framed histograms) and were interpreted as cases where the colloidal fraction was small, and the sampling or measurement variability was high relative to the mean value of these elements.

The elements appear to be divided into two groups. The first group includes the elements C, Si, Al, Fe, Cr, Mn, and Zn, which depending on the sampling time include significant amounts in both the dissolved and colloidal phases. The second group of elements contains Ca, K, Mg, Ba, and Cu, which do not exhibit a loss of concentration after centrifugation and are therefore primarily in a dissolved state (Figure 4).

Distribution of Colloidal C, Si, Al, and Fe throughout a Storm Event. C, Si, Al, and Fe account for most of the elements measured in the colloidal fraction. Working from the assumption that close to 100% of the colloids are composed of these elements the relative composition of colloidal material during a storm event can be obtained by calculating the differences of concentrations before and after centrifugation of each element and then normalizing to 100% (Figure 5). During background conditions (BG) colloids are largely composed of silica. During the storm event, colloidal composition in the urban waterway varies with times. As rainfall begins, the composition of colloids shifts to carbon-containing particles and, initially, aluminum and iron. The carbon content of the colloidal phases increases as the storm continues. However, at peak flow, colloidal silica again predominates, and significant quantities of colloidal iron and aluminum are observed. As the flow decreases, carbon and silica dominate the colloidal fractions. The different sources of material and the reasons for which different colloidal materials enter the urban waterway at different times still are unknown. Temporal variability of colloidal materials may reflect differences in upstream sources (e.g. land use areas), each one with a different colloidal chemical signature. Alternatively, the sources of colloidal material may be similar but released at different times during the storm process. Thus, the chemical signature seen at the point of sampling might reflect that of the different loading over time from similar sources. Finally, the colloidal material at any one upstream location may actually represent a composite of materials from surface runoff, soil moisture, and groundwater.

Estimates of the Colloidal Mass Loadings. Characklis and Wiesner (15) have noted that there is a considerable increase over dry weather flows in particulate organic carbon, iron, and zinc as well as an increase in particle number and suspended solids measured in stormwater runoff. Taking into account the water discharge at each sampling time, mass loadings of colloidal and true dissolved materials were calculated and expressed as a percentage of the total loading of each element. During background conditions, virtually all filtered carbon and Cr are dissolved. By comparison, Al and Mn are primarily transported as colloids (100% and 70%, respectively) and 39% of the Si, 74% of the Fe, and 19% of the Zn are carried as colloids. During the storm event, 17% of the C, 32% of the Si, 79% of the Al, 85% of the Fe, 52% of the Cr, 43% of the Mn, and 29% of the Zn were observed to be colloidal.

Since the definition of colloids is according to size, comparison of results from different investigations is often difficult. Thus, the authors define as the total dissolved (including colloidal materials and the truly dissolved material) the fraction less than 0.45 µm (14, 22) or less than 0.4 µm (23−25) or less than 0.2 µm (26, 27). The truly dissolved fraction varies between less than 1 or 10 kD, and the colloidal fraction comprised between 0.45 or 0.4 or 0.2 µm and 10 or 1 kD is expressed in percentage always relative to the total dissolved. Published estimates of the magnitude of the colloidal fractions in freshwaters are rare (14, 28). Grout and Parron (14) have reported that 40% of the silica in the <0.45 µm filtrate of tropical rivers draining podzols was present as colloids. In rivers draining ferrallitic soils in the same climate area, these same authors have also shown that silica is mainly transported in the dissolved state. Brays Bayou is located in a subtropical area and drains vertisols. The colloidal state of silica in rivers appears to depend strongly on the type of soils and related factors such as climate. The colloidal percentage of Fe in the total dissolved of estuarine and seawater is typically high, and previous investigators have reported values similar to those we observed in urban stormwater: 20−40% in the North Atlantic Ocean (23), 87% in the Venice Lagoon (24), 90% in the Narragansett Bay (26), >85% and around
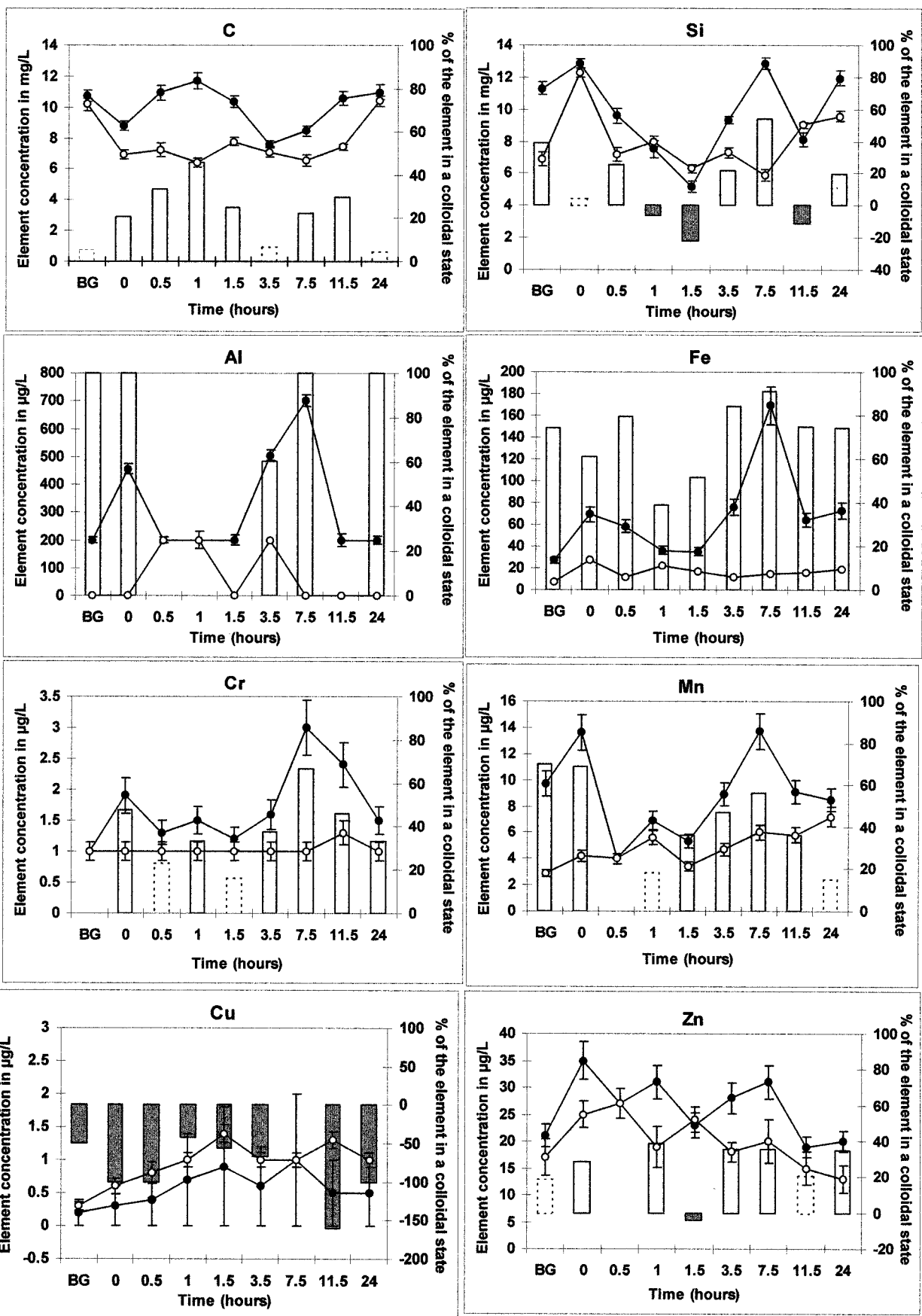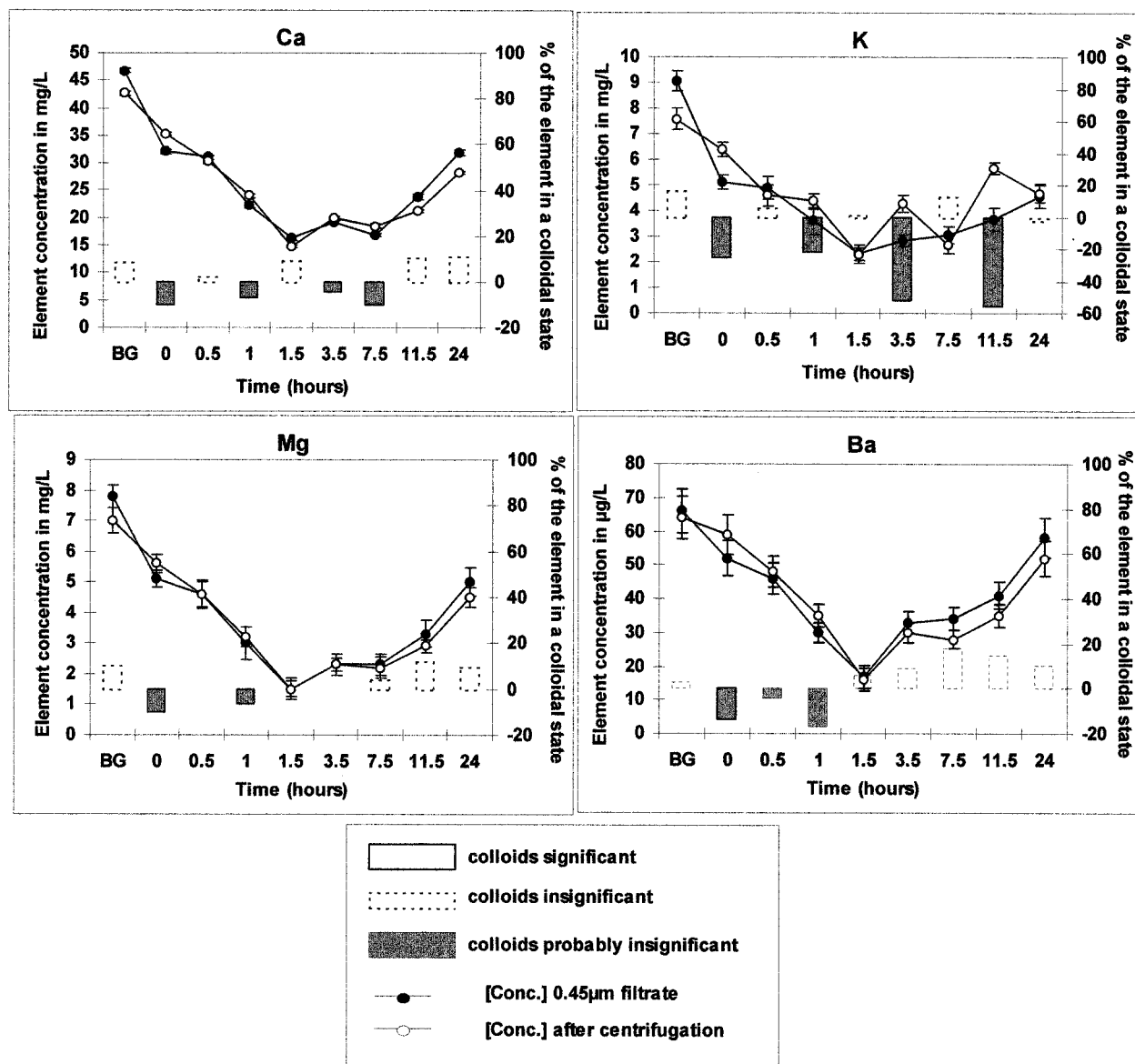
FIGURE 4. Element concentrations of 0.45 μm filtrates (dark circles), after ultracentrifugation (white circles) and % of colloidal material (histograms) throughout a storm event (BG = background conditions, see text for the definition of the significance of colloids, error bars correspond to standard deviations to the mean).
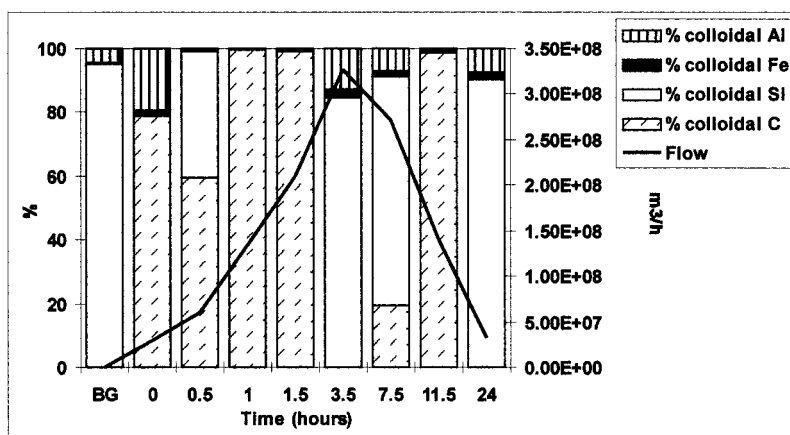

FIGURE 5. Distribution of the colloidal elements and water discharge during a storm event (BG = background conditions).

79% respectively in San Francisco Bay (27) and Gavelston Bay (25 cited by 29). Significant fractions of colloidal Al and Mn have also been reported in these systems (24, 27).

Values of colloidal zinc can vary greatly from one system to another or even within the same system. For example, colloidal zinc in Narragansett Bay (22) ranged from 2 to 20%
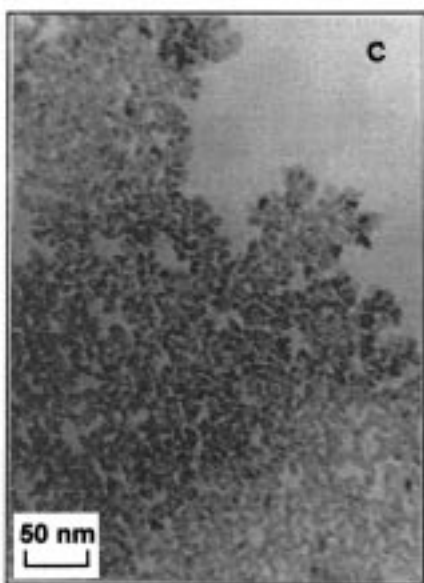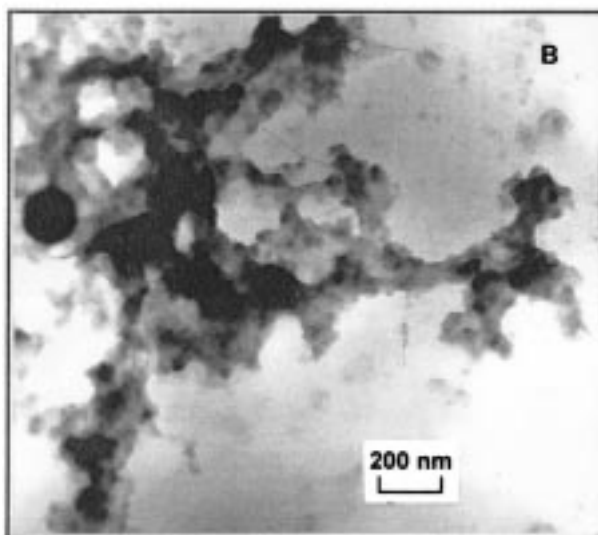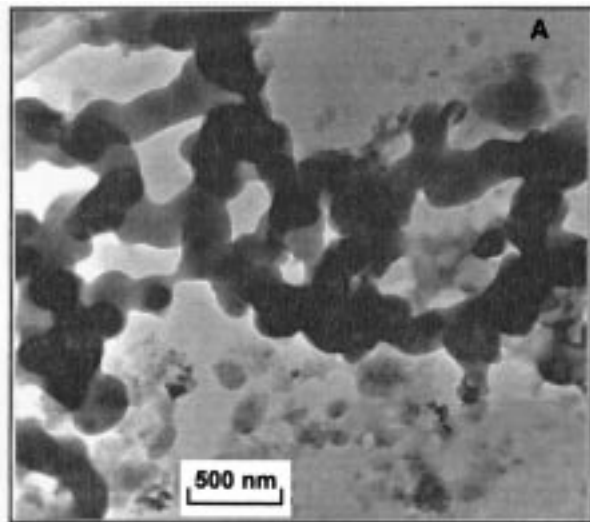
FIGURE 6. Morphological and textural aspects of the colloids extracted from Brays Bayou waters during a storm event: (A) aggregate of rounded entities connecting by bridges ($t = 7.5$ h), (B) anastomosed diffuse domains ($t = 0$ h), and (C) small globules with diameter around 10 nm aggregated together ($t = 11.5$ h).
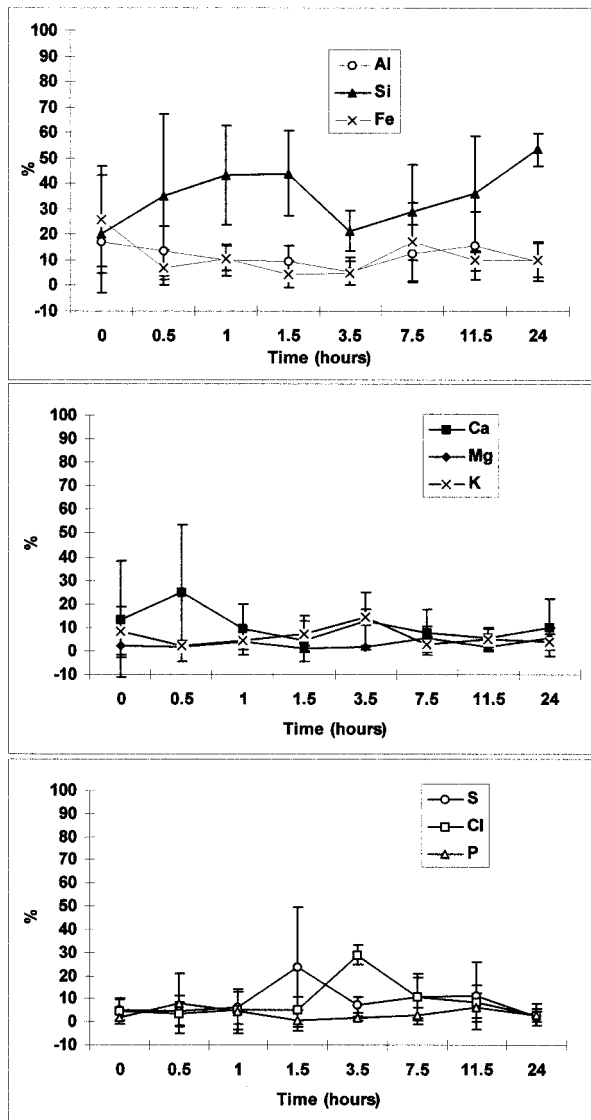

FIGURE 7. Average relative chemical composition of colloids obtained from micro analyzes by EDS ($n = 10$) normalized to 100%.

close to our estimate of 29% and was estimated to be as high as 91% in Gavelston Bay (25). In estuaries colloids are reported to account for one-third to one-half of the Cu in these systems (24, 25 cited by 29, 26, 27). In our freshwater system, Cu was mainly dissolved, but the concentrations were too low (less than 1.5 μg/L) and the standard deviations too high to yield accurate estimates of the colloidal fraction by this technique.

Morphological and Chemical Characterization of the Colloids. Different morphologies of the colloidal phases were observed by TEM including crystallized phases (clays, oxi-hydroxides) and amorphous phases (aggregates, isolated globules, gels). It is difficult to quantify the contributions of each of the colloidal phases by microscopic observation, but, qualitatively, the amorphous phases (aggregates, isolated globules, gels) appeared to be the most abundant. The aggregates were composed of a high number of grains with diameters ranging between 150 and 500 nm and connected by bridges (Figure 6A). The gel-like structures are anasto-mosed in diffuse domains (Figure 6B). Small globules with diameters around 10 nm were also observed isolated or as aggregates (Figure 6C).

Microchemical analysis of a small number of randomly selected colloids, observed by electron microscope, was used to estimate colloidal composition as a basis for comparison
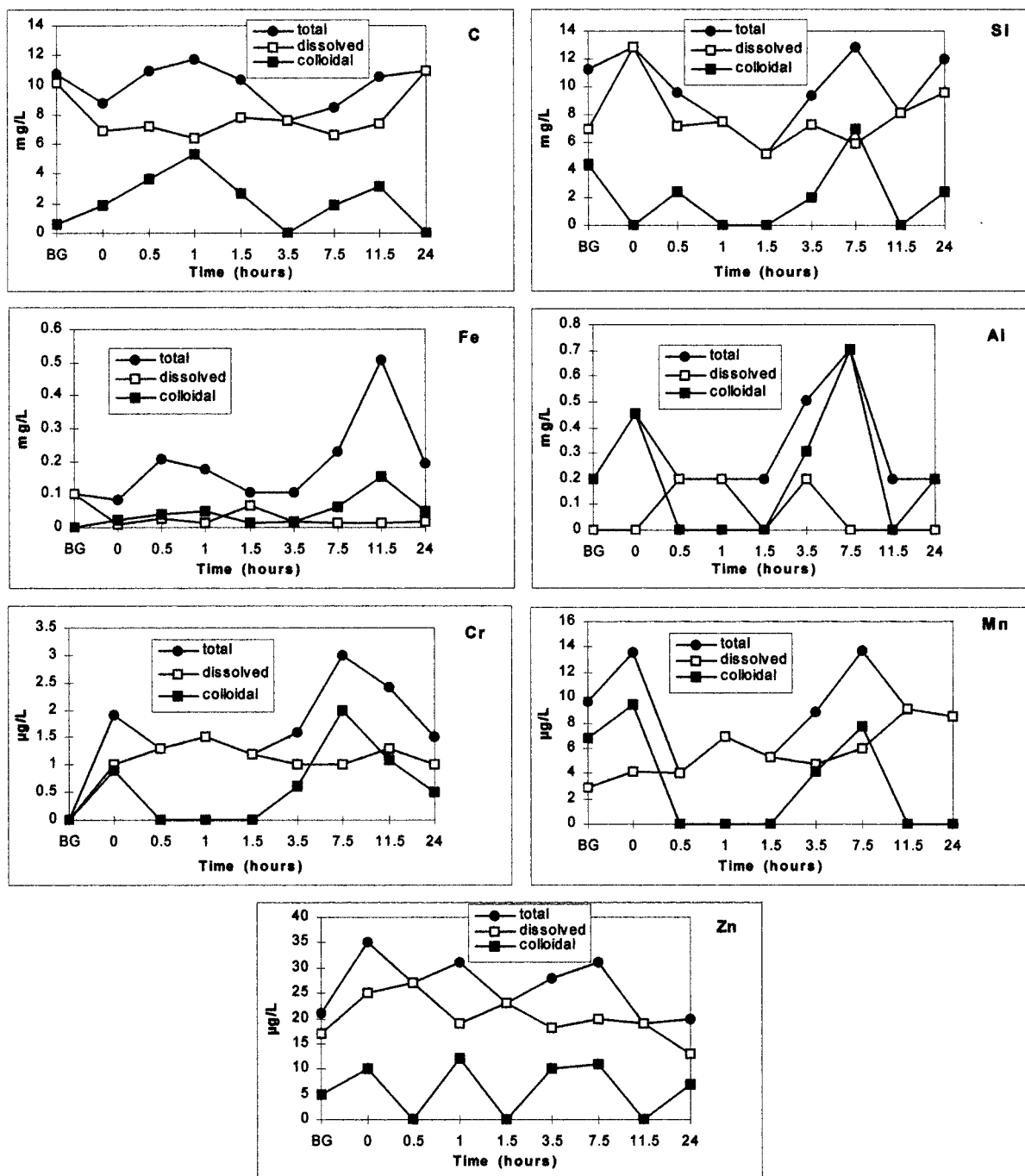
FIGURE 8. Element concentrations in the total, dissolved, and colloidal fractions.

with ICP measurements. Microchemical analysis by dispersive energy spectroscopy of the colloidal particles observed is limited by the inability to measure the carbon content. A lack of detectable elements within a particle is interpreted as an indication that the particle is carbon-rich. Overall, the most striking characteristic of the amorphous colloids was their chemical heterogeneity. Si was the dominant element (on average 35%) over the storm event (Figure 7) followed by Al (on average 12%), Fe (11%), Ca (11%), and S (9%). The elements Cl, K, Mg, and P were detected but in relatively low quantity averaging 9, 6, 3, and 3%, respectively. The standard deviations of these averages are high and suggest a high chemical variability of the colloids in the stormwater itself or over time. The dominance of the elements Si, Al, and Fe in the colloids analyzed by TEM/EDS, is consistent with the ICP analyses. Ca, K, and Mg were detected in the colloids

analyzed by TEM/EDS, whereas ICP measurements suggest that theses elements are largely present as dissolved species. The elements S, P, and Cl were not analyzed by ICP.

At $t = 1$ h when the percentage of colloidal carbon is high, large aggregates constituted by globules of less than 100 nm diameter were often observed. No elements were detected by EDS, and thus it is reasonable to assume that these aggregates are mainly organic. Also no elements were detected on the small globules shown on Figure 6C suggesting that they are also largely organic.

Quantification by ICP analysis as well as morphological and chemical characterization by means of electron microscopy of the colloidal material in Brays Bayou stormwater indicate substantial changes in composition and structure of colloidal materials during the storm event. These changes can be summarized by considering the quantitative contri-

bution to the colloidal fraction to the total amount of each element in the 0.45 μm filtrate.

Influence of the Colloidal Matter on the Chemical Composition of Waters. When the concentrations of dissolved and colloidal elements are plotted together (Figure 8), peaks in the total concentration are seen to correspond to peaks of elements in the colloidal fraction in the cases of C, at $t = 1$ and 11.5 h, and Si, Fe, Al, Cr at $t = 7.5$ h. These elements appear to maintain more or less constant concentrations in the dissolved fraction throughout the storm event. For example, the background concentrations of C and Si remained near 7 mg/L, while Fe and Al were about 20 μg/L and 0.1 mg/L, respectively, throughout the duration of the storm. Variation in the filtered concentrations were largely a function of the variations in the amount of colloidal materials. Moreover, the behavior of the dissolved fraction, when colloids are significant, may be completely different from that of the dissolved fraction in the absence of colloids. For example, the dissolved concentrations of the elements Ca, K, Mg, and Ba, which have no significant colloidal fraction, tend to decrease with increasing flow. Current theory provides no basis for predicting the relative quantities of colloidal species in complex environmental systems. These observations underscore the need for more precise methods for separating and quantifying colloidal materials as well as the need to account for a variety of colloidal phases to accurately describe the speciation, transport, and fate of chemical species in these systems.

Acknowledgments

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