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COLLOIDAL CONTAMINANTS IN URBAN RUNOFF

M.R. Wiesner, G. Characklis, and D. Brejchová
Department of Environmental Science and Engineering
Rice University
P.O. Box 1892
Houston, Texas 77251
phone: 713-285-5129

INTRODUCTION

Rivers typically account for the largest single sediment input to lacustrine and estuarine systems. Pesticides, metals, chlorinated hydrocarbons and other contaminants sorbed to particles carried by rivers may be transported to the sediments of lakes and estuaries. Urban runoff is often an important non-point source of particles to surface waters. For example, under average conditions, over 40% of the suspended solids entering Galveston Bay are estimated to originate from high density urban and residential non-point sources and, in some cases, the fractions of specific contaminants entering Galveston Bay associated with these particles (such as oil and grease) approach 100%[1].

Information on the size distribution of particles in urban runoff has been surprisingly limited despite its importance in providing a strategy for pollution control. While many studies have been done on urban runoff, in only a few instances has the role of specific particle fractions as transport vectors for pollutants in urban runoff been considered.

In this paper, we summarize field data on particle size distributions and contaminant concentrations in urban runoff and streams obtained over a 2-year period. Much of the previous research done in this area has concentrated on particles, larger than10 µm in diameter. While larger particles may represent a significant fraction of suspended materials, we show that the majority of the particles and particle surface area in runoff from one urban center resides within the smaller size fractions.

Inextricably linked to the problem of pollutant transport is the question of whether or not there is significant aggregation of particles in the runoff stream. The degree of aggregation that occurs in the runoff stream will directly affect the fate and transport of the particles, and thus the pollutants sorbed to them. For example, if sub-micron particles aggregate significantly in the runoff stream, particle settling rates will be accelerated in lakes and estuaries, as will the transport of particles and associated contaminants to the sediments.

METHODOLOGY

An urban waterway (Brays Bayou) and several of its tributaries were sampled over a two year period. Brays Bayou drains areas of Fort Bend and Harris counties in Texas within the Houston metropolitan area. The watershed selected as a study area for this research begins at the start of Brays Bayou in west Houston and continues down through southwest Houston until the Bayou reaches South Main St. This portion of the watershed equates to a drainage area of approximately 92 sq. mi. The majority of the watershed is under stress from a wide variety of urban uses consisting mostly of residential and commercial properties. Research was concentrated primarily on four sampling sites. The sites are, from west to east; 1) Keegan's Bayou at Roark Rd., 2) Brays Bayou at Gessner, 3) Poor Farm Ditch, and 4) Brays Bayou at Main Street.

Samples were obtained by dropping a 12-quart, detergent cleaned, polyethylene bucket into the center of the runoff stream from overpasses spanning the Bayou. The bucket containing the sample was retrieved by means of a rope attached to the handle. Approximately one liter of sample was retained in two 500 ml polyethylene bottles. Each bottle had been washed with Alconox® cleaner, rinsed three times with distilled water and then given three final rinses with Milli-Q®, deionized water. Samples were transported back to the lab for analysis. Surface water samples were obtained under both storm and ambient conditions. Upon returning to the lab, all samples were analyzed for turbidity, pH, particle size distribution, total suspended solids (TSS), total organic carbon (TOC), and a suite of metals. Particle size analyses were performed using an electronic particle counter (Coulter Electronics Ltd., Luton, England). The Coulter Multisizer operates on the electronic sensing zone (ESZ) principle. The effective measurement range for such devices usually varies from 2-60% of the orifice diameter. A 19µm orifice tube was used for these experiments with an effective measurement range of approximately 0.5 to 15 µm. Samples were also filtered through various size membranes in order to analyze the composition of the filtrates in each size fraction. The filtration system consisted of four 250 ml vacuum filter holders (Nalgene, Prod. 315-0047) mounted on 1000 ml Erlenmeyer flasks. Each flask was connected to a vacuum pump (Gast, No. 1HAB25BM100X) by means of Tygon® (R-3603) tubing. The cutoffs for membranes used in the fractionation procedure were reported by the manufacturer to be 0.45 µm, 0.1 µm and 10^5 daltons. All of these membranes are cellulose nitrate filters (Sartorious AG, Goettingen, Germany, 47 mm circular).

Membrane-fractionated samples were analyzed for suspended solids, TOC, and metals. All determinations of suspended solids were made according to procedure 2540D in Standard Methods[2]. In the best cases, solids measurements yielded data on the mass of particles in the size ranges >20 µm, 0.45 to 20 µm, 0.1 to 0.45 µm and 10^5 daltons to 0.1 µm. Unfortunately, it was often difficult to obtain data for the smallest size range, as the 10^5 dalton filter would frequently foul to the extent that filtration was not possible.

In preparation for metals analysis, each filtrate was concentrated through a Nitric Acid-Hydrochloric Acid Digestion, method 3030F in Standard Methods[2]. Digestion resulted in concentrating the samples 5-10 times. Samples were stored in detergent washed, acid rinsed glass vials and refrigerated at 4°C until analysis. Metal concentrations (Fe, Sr, Ba, Pb, Zn, Ca, Cu and Mn) were measured by Inductively Coupled Plasma (ICP) -Atomic Emission Spectrometry (Perkin-Elmer).

Samples were also obtained for the purpose of evaluating particle aggregation under controlled conditions. In aggregation experiments, "background" or storm water was transported back to the laboratory, and the largest particles were allowed to settle from suspension. The supernatant was then transferred to a 2-liter beaker and mixed at a prescribed speed. Mixing conditions as a function of paddle rotational speed were known for this system. An rpm was selected toprovide the mean velocity gradient, G, of approximately 70 per second estimated to occur in the bayou under stormwater flow conditions. Particle size distributions were measured at regular time intervals to evaluate the kinetics of particle aggregation in the system and to quantify the collision efficiency factor, α.

Aggregation was further investigated by following a plug of water in Brays Bayou from the west side of Houston through the Houston Ship Channel. During this phase of the project, three more sampling sites were added to the four used for stormwater sampling ; Brays Bayou at Old Spanish Trail, Brays Bayou at the Houston Ship Channel, and the Houston Ship Channel at the San Jacinto Monument. The Houston Ship Channel represented the last leg of stormwater travel from Houston to the Galveston Bay. It is an unconcreted, man-made channel approximately a half mile wide by the time it reaches the San Jacinto Monument. Particles from Brays Bayou have been significantly obscured by dilution and subsequent industrial additions by the time they reach this point. There is also a significant increase in salinity at this sampling location due to its proximity to the Bay. These samples were analyzed for pH, turbidity, particle size distribution, fractional organic carbon and fractional metals in the same manner as those measured during the stormwater phase of this work.

RESULTS

Particle size data show that more than 90% of the particle number exists between 0.45µm and 2µm. Photon Correlation Spectroscopy measurements also show a peak in the distribution varying from 0.4µm to 0.7µm. Particle size distributions in runoff were taken under both storm and ambient conditions. Although the profiles under both sets of conditions were similar, the concentration of particles in the storm samples was much higher, both in particle number and calculated particle surface area (Figure 1). These higher concentrations, coupled with much higher flow rates in the runoff stream during a storm event, produce high particle loadings during storm events.

TOC analysis indicated that the particulate phase was composed of 1 to 10% organic carbon. Functional groups on particulate organic carbon may complex metals and enhance the transport of metals with particles. Under storm conditions TOC concentrations increased as the bayou water progressed downstream. TOC tended to be bimodally distributed between the largest and smallest (dissolved) size fractions (Figure 2). Thus, metals readily complexed by TOC would also be expected to exhibit a bimodal distribution with respect to size fraction.

Metals analysis of the samples yielded detectable levels of Fe, Ba, Cu, Mn, Pb and Zn. The metals concentrations in the runoff, expressed per mass of suspended solids, were comparable with concentrations reported in previous studies evaluating the metals content of Galveston Bay sediments. With regards to all metals analyzed, except Zn, there was good correlation between the profiles of the runoff samples and the Bay sediments. While elevated concentrations of zinc have been reported in the

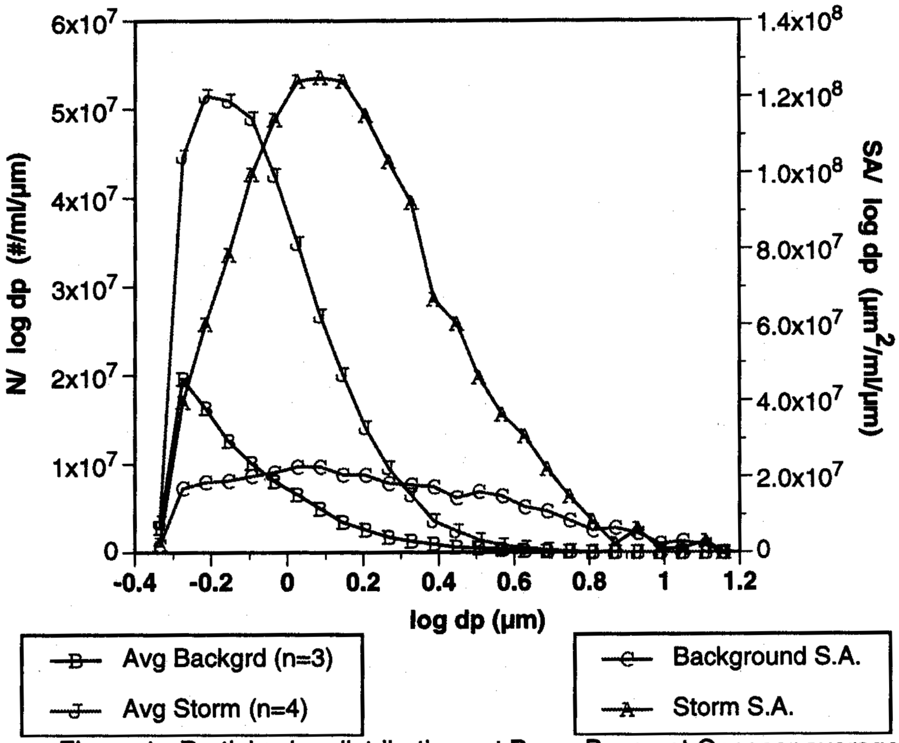

Figure 1. Particle size distributions at Brays Bayou at Gessner averaged over 3 sampling dates for background conditions and 4 separate storm events.

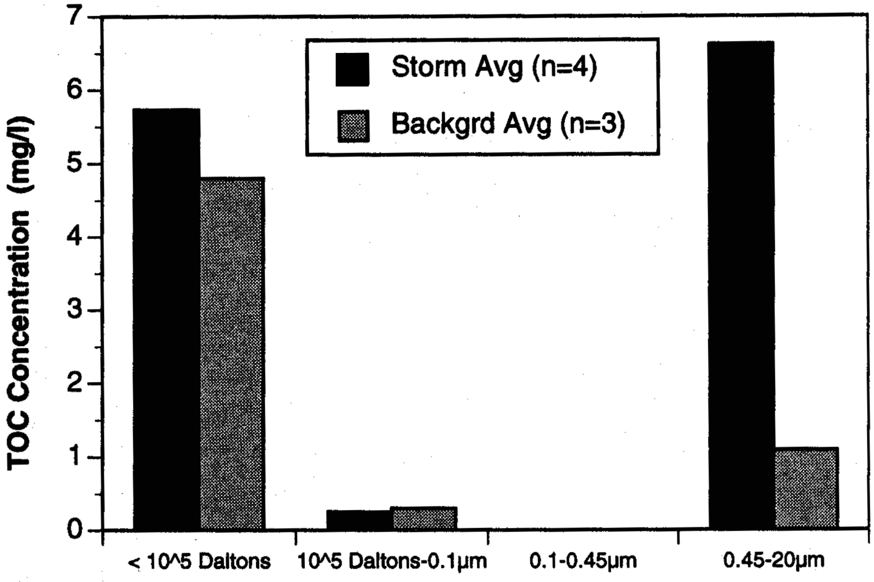

Figure 2. Size fractionation of TOC in Brays Bayou at Main Street averaged over 3 background samples and 4 storm events.

runoff from other urban centers, it remains to be determined why enriched concentrations of zinc apparently are not observed in the sediment record for Galveston Bay. Zinc, like barium and strontium displayed a bimodal distribution with respect to size fraction (Figure 3). However, unlike zinc, barium and strontium decreased in concentration during storm events relative to the background concentrations observed.

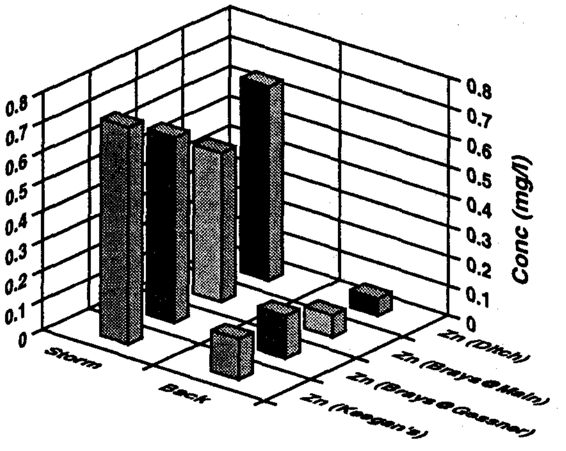

Figure 3. Variations in average zinc concentrations during storm and background conditions at the four sampling sites.

Intensive sampling of individual storm events produced a similar picture of the materials loadings to this urban waterway. Different fractions of materials were "eluted" to the bayou at different times during storm events. For example, larger particles tended to peak in concentration earlier during a storm than did smaller particles. This is reflected in the data summarizing settleable (within 15 minutes) and unsettleable suspended solids as compared with particle number concentrations (Figure 4). Similarly, metals tended to peak in concentrations at different times. Iron concentrations peaked at approximately the same time as the unsettleable solids (4 to 8 hours) and remained above background concentrations for at least 24 hours after the onset of the storm. In contrast, zinc concentrations peaked at 4 hours and then decreased to, or below, background concentration. Although zinc and TOC concentrations correlated significantly ($r^2 = 0.8$) TOC concentrations were observed to remain above background levels for at least 24 hours after the onset of the storm events monitored.

Laboratory simulations of mixing and particle aggregation in Brays Bayou indicated that significant aggregation is likely to occur in runoff water within 1-3 hrs. The number concentration of particles measured by the particle analyzer with a 19 μm orifice increased consistently to a maximum in the first few hours of mixing. Particle number then displayed a drop back down to approximately the original concentration, eventually settling into a slow, steady decline. After 24 hours of continuous mixing in the lab, large aggregates of particles were readily visible. The original increase in particle number is attributed to the aggregation of particles which are initially below the 0.45μm threshold of the particle analyzer. As these particles reach the threshold there is a rise in the number of measurable particles. However, a monotonically decreasing number concentration was observed in aggregation experiments when particle concentrations were measured using a 50 μm orifice. Because this orifice provides a window on a slightly larger fraction of particles, the effect of aggregation into the smaller size classes observed with the 19 μm orifice is masked. A least-squares fit to a semi-log plot of particle concentration yields values of the collision efficiency factor on the order of 10^{-2} (Figure 5).

Although it is evident from laboratory mixing studies that significant aggregation of particles entering the bayou is probable, aggregation was not evidenced in samples obtained following a a single plug of water down the bayou; particle size distributions remained largely unchanged with distance. Aggregation of particles present in the upper reaches of the bayou may be masked by the introduction of particles from the numerous small tributaries that feed into Brays Bayou as it makes its way through the city.

CONCLUSIONS

The number and surface area concentrations of particles in the urban runoff studied were dominated by particles 2 to 5 μm in diameter. Zinc and barium were observed to be distributed bimodally with respect to the size fractions where they predominate, while lead and iron tended to associate almost exclusively with the largest size fraction. Most metals are associated with size fractions either larger than 0.45 μm or less than 10^5 daltons. This bimodal distribution of metals is similar to that observed for total organic carbon. Materials in different size classes were observed to reach a maximum in concentration at different times during a storm, larger particles reaching their maximum concentration before smaller particles.

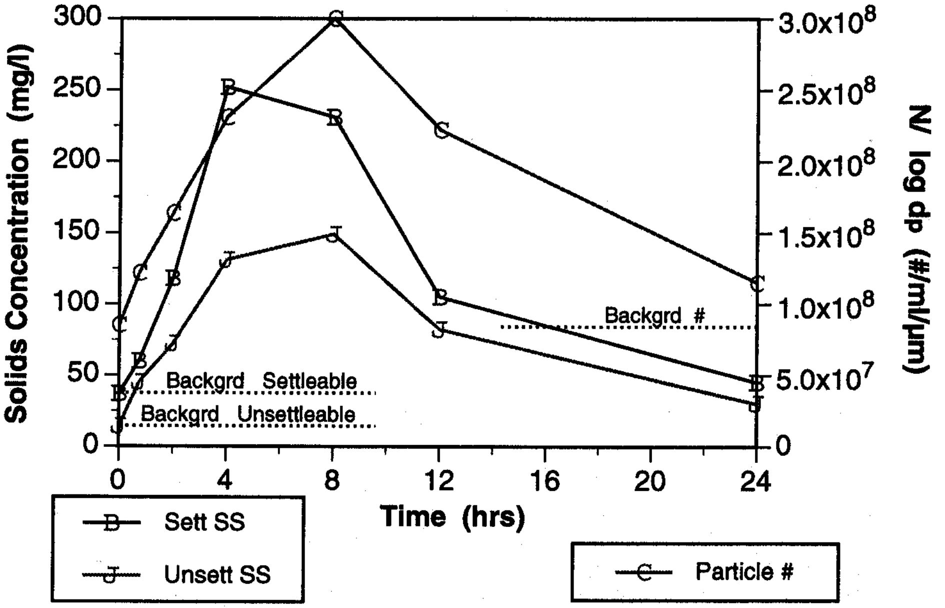

Figure 4. Comparison of suspended solids and particle number concentrations in Brays Bayou at Main Street on 27 August 1993.

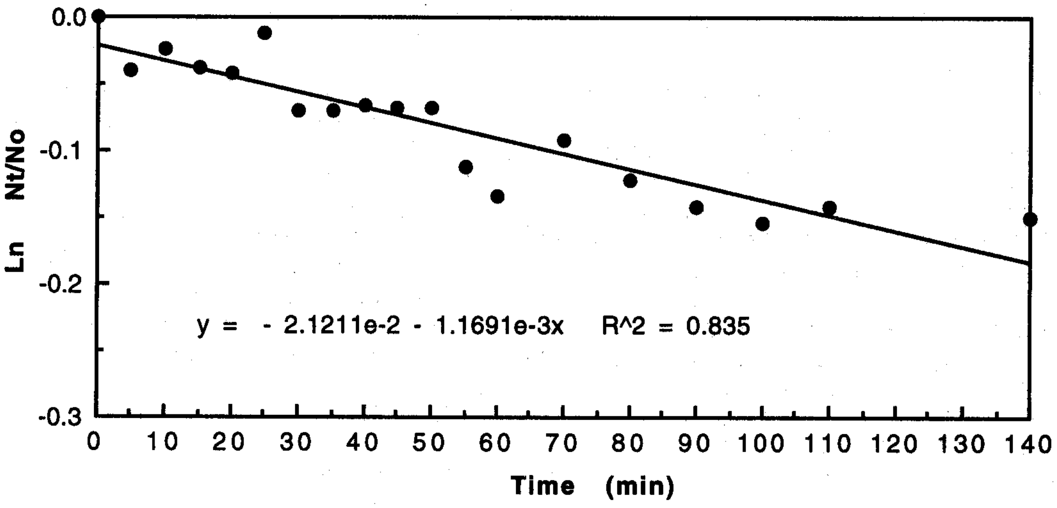

Figure 5. Log particle number concentration (normalized to initial concentration) in Brays Bayou at Main Street during storm event on 12 May 1994.

LITERATURE CITED

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MODELLING AIR EMISSIONS FROM CONTAMINATED DREDGED MATERIALS

L J Thibodeaux[1], K T Valsaraj[1], D D Reible[1] and J M Brannon[2]
[1]Department of chemical engineering,
Louisiana State University, Baton Rouge, LA 70803
[2]U S Army Waterways Experiment Station,
Vicksburg, MS

INTRODUCTION:

A confined disposal facility (CDF) is a diked area for gravity separation and dredged material solids. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals (VOCs) associated with the sediment to be released to the air. Sediments from the New Bedford Harbor (NBH) Superfund Site, MA, contain significant amounts of polychlorinated biphenyls (PCBs), some of which may be released to the air during evaporative drying in a CDF.

Models for evaluation of volatile emissions to air during dredged material disposal have been developed (Thibodeaux, 1989). These theoretical models may be applied to calculate potential PCB emissions from CDFs proposed for containment of NBH sediment. Four locales associated with a CDF operation were identified as separate volatile sources. These locales were: (1) the sediment (dredged material) relocation locale, (2) the exposed sediment locale, (3) the ponded sediment locale and, (4) the vegetation-covered sediment locale. The exposed sediment locale was ranked the highest. Field or laboratory emission data suitable for comparison to model predictions were not available for any of the locales. Brannon (1989) reported some preliminary data for locale 2 for the emission of Aroclor-1242 from a drying sediment exposed to air under laboratory conditions. This paper compares the experimental values against theoretical predictions.

METHODOLOGY:

A series of four experiments were performed with an emission isolation flux chamber. This apparatus was placed atop the sediment to collect the PCB vapors as air was passed over the sediment in the chamber for 1 hour. The vapors were trapped in fluorisil tubes and analyzed by gas chromatography. Two adsorption tubes, and an air rate of 900 cm^3/min were used. In general the experiments can be placed into two classes, wet and dry. The first three experiments were performed with sediment saturated with water; these are called *wet sediment experiments*. The last experiment showed significant cracking and drying of the surface sediment. The soil porosity decreased from 0.774 on day 1 to 0.103 on day 10, while the solid fraction increased from 0.33 to 0.88 during this period. The laboratory was maintained at 20±0.3 °C and low relative humidity throughout the experiment. The experiment number 4 shall be termed the *dry sediment experiment*.

The following is a brief presentation of the model that applies for the exposed sediment locale. Contaminated sediment that is wet and exposed directly to air results in the highest VOC emission rates. VOCs sorbed on the particles at the soil surface have a relatively short pathway to the air. The top layers eventually become depleted of the chemical. Continuing losses will come from within the soil pores. The following equation applies for this transient volatilization rate

$$N_A = \frac{W_A K^* - C_a}{\left[\dfrac{\pi t}{D_{Aa}\left(1 + \dfrac{\rho_b}{\epsilon_a K^*}\right)}\right]^{1/2} + \dfrac{1}{k_A}} \qquad \textbf{(1)}$$

where N_A is the emission flux from the soil ($\mu g.m^{-2}.h^{-1}$), K^* is the air/soil partition constant ($g.m^{-3}$), W_A is the chemical concentration on soil ($\mu g.g^{-1}$), t is time (h), D_{Aa} is the diffusion constant of the chemical in the air-filled pores ($m^2.h^{-1}$), ρ_b is the soil bulk density ($g.m^{-3}$), ϵ_a is the air-filled porosity ($m^3.m^{-3}$), k_a is the air-side mass transfer coefficient ($m.h^{-1}$), and C_a is the chemical concentration in the background air ($\mu g.m^{-3}$). The above equation is for an