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Fog chemistry in the Texas–Louisiana Gulf Coast corridor

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Abstract

Fog samples were collected in two population centers of the US Gulf Coast (Houston, Texas and Baton Rouge, Louisiana) using Caltech active strand cloud collectors. A total of 32 fogwater samples were collected in Baton Rouge (November 2004–February 2005) and Houston (February 2006). These samples were analyzed for pH, total and dissolved organic carbon, major inorganic ions, and a variety of organic compounds including organic acids, aromatics, carbonyls, and linear alkanes. Fogs in both environments were of moderate density, with typical fog liquid water contents $< 100 \text{ mg m}^{-3}$. Fog samples collected in Houston reflect a clear influence of marine and anthropogenic inputs, while Baton Rouge samples also reflect agricultural inputs. The volume-weighted mean fog pH was somewhat more acidic (~ 4.3) in Houston than in Baton Rouge (~ 5.0). A wide pH range was observed in fog at both locations. Houston fog had higher concentrations of Cl^- , NO_3^- , Na^+ , Mg^{2+} , and Ca^{2+} . Sulfate to nitrate ratios were high in fogs at both locations, typical of many clouds in the eastern US. Total organic carbon concentrations were much higher in Houston fogs than in Baton Rouge fogs. Efforts to speciate dissolved organic carbon (DOC) reveal large contributions from organic acids and carbonyls, with smaller contributions from other organic compound families including aromatics, alkanes, amides, and alcohols. Approximately 40% of the fog DOC was unspicated in samples from both study locations.

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1. Introduction

The Gulf Coast area between Houston (Texas) and Baton Rouge (Louisiana) is heavily industrialized. This corridor has the largest concentration of

petrochemical and chemical operations in the United States. Extensive shipping and transportation activities and several large population centers contribute to air pollution in the region. Agricultural activities also influence air quality in this area. Rural areas in Texas and Louisiana utilize a variety of agricultural practices that emit pesticides, herbicides, and insecticides. Overall, this region of the United States is known to experience significant air

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pollution problems (Russell et al., 2004; Burby, 2000).

Air pollutants migrate across this corridor and undergo wet and dry deposition. The National Atmospheric Deposition Program (NADP) has carried out rainwater analysis for a decade or more at research stations in Texas and Louisiana. Rainfall intensity, pH, conductivity, and the main inorganic ion components (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , SO_4^{2-} , NO_3^- , and Cl^-) are monitored weekly at these sites. Mercury deposition measurements have recently been added. Organic species are generally not measured. Dry deposition measurements are also not routinely made across much of this region and measurements of fog chemistry, and associated occult deposition, are absent entirely.

Fog is a common occurrence in this part of the United States. Fig. 1 summarizes the occurrence of fog in Baton Rouge and Houston from 1996 to 2004. Most fog occurs in the cooler months of the year, from October through March. Overall fog frequency is a little higher in Baton Rouge than in Houston. Although different types of fog are possible, radiation fog is the most common. Fogs consist of droplets ranging in size from a few micrometers to several tens of micrometers, each formed by water vapor condensation onto an aerosol particle that serves as a cloud condensation nucleus (CCN) (Rauber, 2003). The chemical compositions of the particles acting as CCN determine the initial compositions of the fog droplets, which can be further altered by uptake

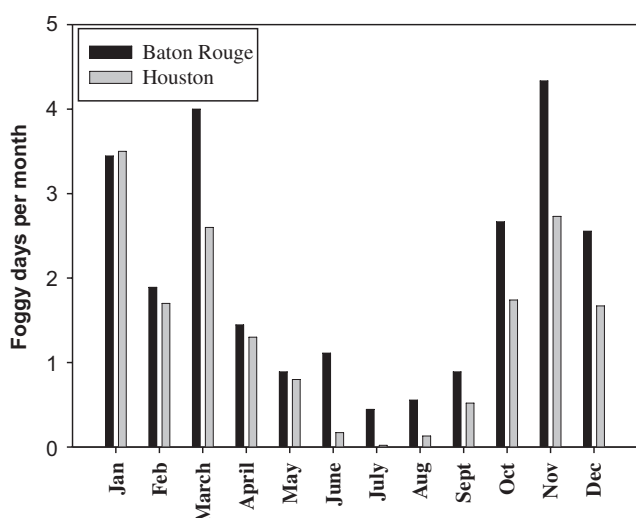


Fig. 1. Number of foggy days per month in Baton Rouge, LA and Houston, TX, during 1996–2004 (data obtained from National Climatic Data Center, NOAA).

of soluble gases and by aqueous phase chemical reactions. As fog drops settle to the ground, the pollutants contained within them are deposited (occult deposition). When fog dissipates, it leaves behind a portion of the scavenged pollutants on residual aerosol particles. The enhancement of fog formation by high aerosol concentrations, followed by the growth of these particles during fog processing, has been referred to as a smog–fog–smog cycle. While it has been clear for several decades that fogs are active processors of inorganic atmospheric pollutants, it has become evident in recent years that many organic species, both gas and particle phase, also interact strongly with fogs (Chen et al., 2007; Raja et al., 2005; Collett et al., 2001). In order to improve our understanding of pollution processing occurring in fogs and their potential effects on human health and the environment, it is imperative that we learn more about fog composition.

Fogwater characteristics have been reported for several regions of the world. Extensive analyses of fog have been made in California's Central Valley (Jacob et al., 1986; Collett et al., 1999; Zhang and Anastasio, 2001), in the Los Angeles Basin (Munger et al., 1983), along the northeast Atlantic Coast of the United States (Klemm et al., 1994), in Italy's Po Valley (Fuzzi et al., 1985), in Dubendörf (Switzerland) (Czuczwa et al., 1989), and in Strasbourg (France) (Millet et al., 1997) over the past two to three decades. Much of the information gathered has focused on fog pH and inorganic ion composition. Fog also contains substantial amounts of organic species; however, the identification of these compounds is far from complete. A handful of compounds such as low-molecular weight carboxylic acids, linear alkanes, pesticides, aromatic hydrocarbons, oils, and esters have been identified (e.g., Facchini et al., 1990; Capel et al., 1991; Millet et al., 1997; Fuzzi et al., 2002; Herckes et al., 2002a; Loflund et al., 2002; Herckes et al., 2007). Other recent investigations have attempted to characterize organic compounds in fogwater using LC-DAD-MS (Kiss et al., 2001). More recently, surface-active organic compounds (humic- and fulvic-acid-like substances) have been identified in fogwater (Gelencsér et al., 2000; Cappiello et al., 2003). Increasing evidence from recent studies has shown that a considerable fraction of organic carbon is theoretically impossible to speciate because they are made up of humic-like macromolecules. Havers et al. (1998) demonstrated that humic-like substances separated from particulate matter made up

a significant fraction of organic carbon, and can be characterized primarily by polysaccharide and aliphatic substructures.

Information about fogwater composition and fog processing of air pollutants in the US Gulf Coast area is scant. Hence, a collaborative effort was undertaken to collect fogwater from several fog episodes in two different Gulf Coast regions, Baton Rouge and Houston. The collected fogwater was then subjected to several types of chemical analysis, both inorganic and organic. Specifically, we were interested in the following questions: (1) what are the characteristics of fogwater in the Gulf Coast area and how do they compare to other regions in the United States? (2) are there differences between fog composition in the more industrialized Houston area and the metro Baton Rouge area? and (3) do organic species constitute an important fraction of total fogwater solutes in Gulf Coast fog episodes?

2. Experimental methods

Two fog sampling campaigns were conducted, one in Baton Rouge, Louisiana (November 2004–March 2005) and another in Houston, Texas (February 2006). Baton Rouge and Houston often experience similar weather patterns. Both continental and Gulf of Mexico air masses influence weather in the region. While Baton Rouge and vicinity are influenced by both industrial and agricultural activities, Houston is mainly influenced by industrial and urban emissions. The Louisiana State University (LSU) agricultural farm, the location of the Baton Rouge fog collection site, uses ammonia–nitrogen fertilizers at various times during the year. Industrial emissions in Louisiana and the Baton Rouge area include electric power plants, refineries, sulfuric acid production, and carbon black production (La DEQ, 1999).

Fig. 2 shows the locations of the two sampling sites. The site selected for sampling in Baton Rouge was located in open agricultural land maintained by LSU, similar to the site used during a preliminary fog study (Raja et al., 2005). This sampling location is approximately 137 km inland from the Gulf of Mexico. In Houston, fog samples were collected at the Texas Commission on Environmental Quality (TCEQ) Channelview monitoring site in east Houston approximately 40 km inland from the Gulf of Mexico. More information about the site is available at http://www.tceq.state.tx.us/cgi-bin/compliance/monops/site_photo.pl. The site

is located in a primarily residential area with numerous schools. The closest industrial sources are located approximately 1.6 km away and are primarily to the northeast and east. Interstate highway 10 is approximately 4 km south of the site. VOC concentrations are not typically high at this location but episodic rises are noted from time to time due to traffic patterns and industrial activity (Ryerson et al., 2003; Buzcua and Fraser, 2006).

2.1. Sampling methodology

2.1.1. Fog collection and monitoring

Fog samples were collected using various versions of the Caltech active strand cloudwater collector (CASCC) (Demoz et al., 1996). A single stage stainless steel CASCC (ss-CASCC) (Herckes et al., 2002a) was used for collection of bulk fog samples ($D > 3.5 \mu\text{m}$). This collector features stainless steel collection surfaces. Collected droplets flow down through a stainless steel trough into a pre-cleaned amber glass bottle. A stainless steel version of the size-fractionating CASCC (Demoz et al., 1996), an ss-sf-CASCC (Herckes et al., 2002a), was used to collect drop size-resolved samples of fogwater. The ss-sf-CASCC contains two stages in series, with larger stainless steel rods in the first stage and a bank of stainless steel wire in the second stage. The droplet sizes collected with 50% efficiency in the first and second stages are approximately 16 and 4 μm diameter, respectively. As in the ss-CASCC, collected fog droplets drain through stainless steel sampling troughs into pre-cleaned amber glass sample bottles. A three-stage CASCC, designed specifically for this project, was also used for size-resolved fog drop sampling. The three-stage version of the sf-CASCC is similar in design to the sf-CASCC with addition of an additional inlet stage for large drop collection. Fifty percent droplet size cuts of 22, 16, and 4 μm diameter are featured in stages one, two and three, respectively. The performance of this collector was optimized during the design process through two-phase flow simulations using the computational fluid dynamics package FLUENT. Collector materials are polycarbonate with Teflon collection surfaces and sample troughs. Collected fogwater drains into polyethylene sample bottles.

The high-volume atmospheric fogwater collector used previously in preliminary measurements at Baton Rouge (Raja et al., 2005) was placed approximately 0.6 m above the ground. The CASCC

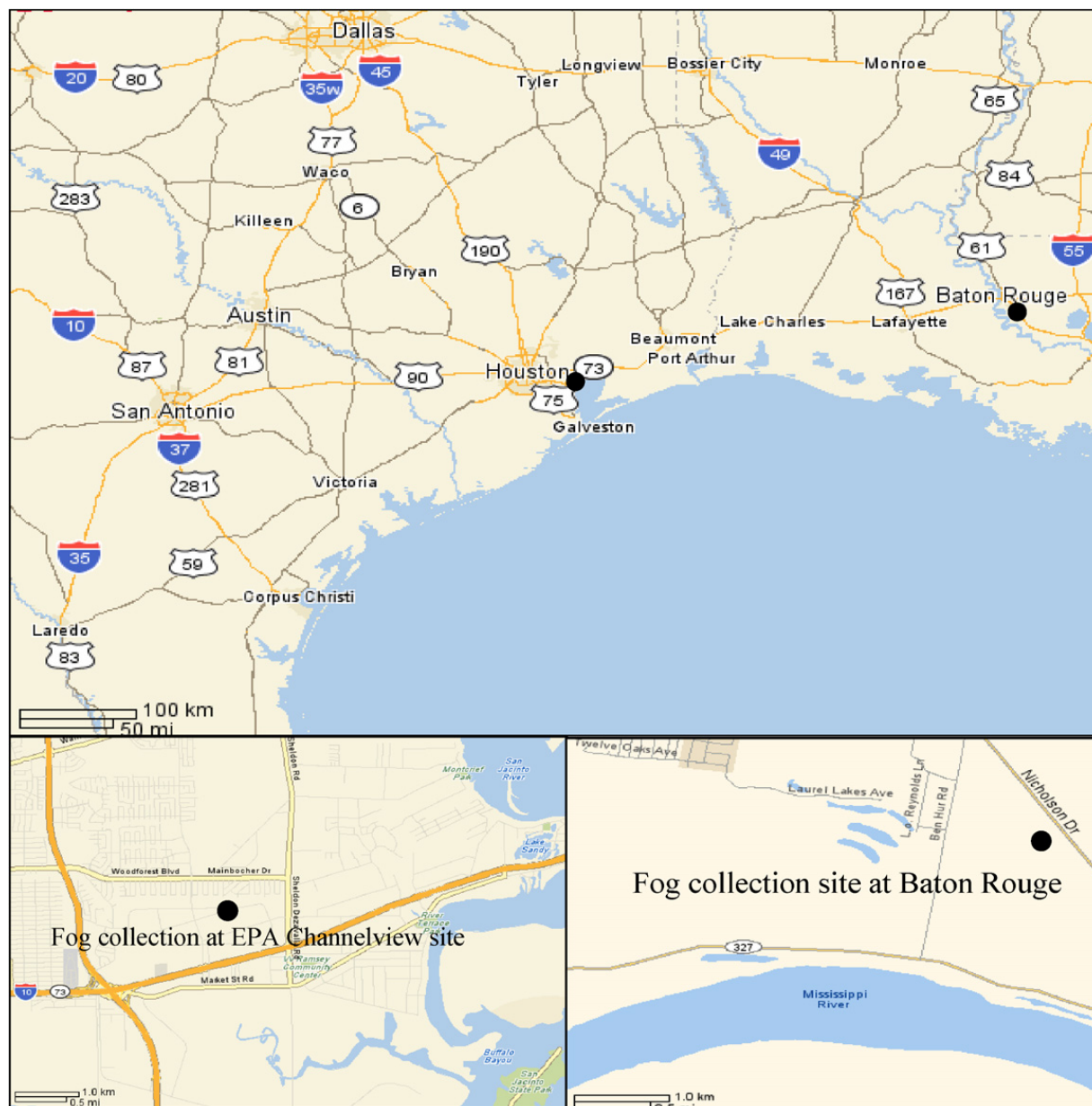


Fig. 2. Approximate location of sampling sites at Baton Rouge, LA and Houston, TX.

collectors used in the fog collection campaigns reported here were placed approximately 3 m above the ground, thus yielding cleaner samples less influenced by soil and insect contamination. The large ss-sf-CASCC, three-stage CASCC, and ss-CASCC collectors used in these later studies also feature much higher air sampling rates (approximately 38, 24, and 19 m³ min⁻¹, respectively) and, therefore, collect much larger volumes of fogwater (volume collection rates can exceed 100 mL h⁻¹ under common conditions).

A Gerber Scientific Particulate Volume Monitor (Model PVM-100) was used to provide continuous measurements of fog liquid water content (LWC).

The data acquisition system connected to the PVM instrument was programmed to page a site operator when fog was detected for a period of 15 min. Once paged, the site operator typically arrived onsite within approximately 10 min to initiate fog collection. The PVM was regularly calibrated for both LWC and particle surface area (PSA) using a manufacturer supplied calibration disk.

2.2. Chemical analyses

Collected fog samples were weighed and sample aliquots were taken on-site for measurement of pH, total and dissolved organic carbon (TOC and

DOC), organic acids, inorganic ions, carbonyls, and other trace organic compounds. The pH was measured using an Orion[®] pH meter and combination electrode. TOC aliquots were stored in pre-cleaned glass vials. DOC aliquots were prepared by filtering fogwater through a pre-baked quartz fiber filter and stored in pre-cleaned glass vials. Aliquots for organic acid analyses were preserved by adding chloroform as a biocide. Carbonyls were preserved by derivatization with dinitrophenylhydrazine (DNPH). Large portions of fogwater samples collected using the ss-sf-CASCC were stored in pre-baked 500–1000 mL amber glass bottles for analysis of trace organic species by GC/MS.

Mono and dicarboxylic organic acids were determined by ion chromatography using a Dionex DX500 system equipped with a Dionex AS11-HC column and guard column, a Dionex ATC-1 Anion trap column, an anion self-regenerating suppressor, and a Dionex CD20 conductivity detector using a sodium hydroxide eluent gradient. Major inorganic anions and cations were analyzed by ion chromatography using two Dionex DX-500 systems equipped with AS4A and CS12A separation columns, anion and cation self-regenerating suppressors and standard eluents with conductivity detection. The TOC and DOC concentrations were determined using a Shimadzu TOC 5000A, where organic carbon in an injected sample is oxidized on a catalyst bed at 680 °C, followed by the measurement of evolved CO₂. The instrument was calibrated with a series of aqueous potassium hydrogen phthalate standards. Carbonyls in the fogwater were analyzed as their DNPH derivatives using an Agilent Model 1050 HPLC with diode array detection. Identification of individual carbonyl components was confirmed by electrospray mass spectrometry using an Agilent Model XCT Ion Trap Mass Spectrometer.

Additional trace organic compounds present in the fog sample were extracted into dichloromethane, concentrated to approximately 200 µL, and analyzed in a gas chromatograph (Agilent Technologies, Model 6890) equipped with a capillary column (30 m long × 0.32 mm o.d., 0.25 µm column i.d.) and a MS5973 mass spectrometry detector. For more details on the sample preparation methodology and GC/MS analysis details, the reader is directed to Raja, 2005.

3. Results and discussion

Table 1 summarizes conditions during fog collection at Baton Rouge for the November 2004–February

2005 study period. There were a total of seven fog events sampled during this campaign. Most of the fog formed late in the night and dissipated during the morning hours. Winds were light during fog collection, with speeds typically ranging from 0 to 3 m s⁻¹ at the Baton Rouge reporting station. The general meteorological conditions during fog collection in Houston/Channelview are also listed in Table 1. Houston fog samples were collected on two consecutive nights on 21 and 22 February 2006, with fog forming late in the night and slowly dissipating by morning hours.

Table 2 summarizes general characteristics of fogwater collected in Baton Rouge and Houston. The average fog LWC in the Baton Rouge fog episodes was approximately 84 mg m⁻³, somewhat higher than the average Houston LWC of 65 mg m⁻³. The volume-weighted mean (VWM) pH of Baton Rouge fog was approximately 4.0, but exhibited a wide range from strongly acidic (2.76) to an alkaline (relative to background atmospheric water pH values of ~5–5.5) pH of 6.37. Houston fogwater samples had a VWM pH of 3.4, with a range from 3.19 to 7.19. The Houston fog VWM TOC concentration of 11.5 mg L⁻¹ was nearly double the Baton Rouge average of 6.0 mg L⁻¹. At both locations, DOC concentrations were only 10–12% lower than TOC, indicating that most of the organic matter in the fog drops was dissolved.

Table 3 lists the ionic composition of fogwater in Baton Rouge and Houston. The average ion balances (cation/anion ratio on an equivalent basis) from the analysis of ionic composition of Baton Rouge and Houston fogwater samples were determined to be 1.11 ± 0.17 and 1.12 ± 0.50, respectively.

In Baton Rouge, the most prevalent inorganic ion was ammonium. Its VWM concentration of 2078 µN was similar to the sum of nitrate (181 µN) and sulfate (1791 µN) concentrations, indicating a rough balance existed between inputs of these inorganic basic and acidic species. Not surprisingly for this part of the country, sulfate concentrations typically far outweighed nitrate concentrations due to the higher concentration of particulate and gaseous sulfur dioxide concentration (Clean Air Status and Trends Network (CASTNET), 2007). The abundance of ammonia at this site reflects significant agricultural activity in the region and possible local influence from the LSU agricultural farm where fog was sampled. The pH of Baton Rouge fogs reflects the relative inputs of ammonia, nitric acid, and sulfuric acid.

Table 1
Description of conditions during fog collection at Baton Rouge, LA and Houston, TX

Date	Conditions during fog	Sampling start/end time	Sampling time (h)	Volume of sample collected (L)	Duration of <400 m visibility (h)	Duration of <200 m visibility (h)	Approximate T ($^{\circ}\text{C}$)	Range of wind velocity (m s^{-1})
19 November 2004 ^a	Overcast	3:15–6:34 a.m.	3.3	0.143	1	0	18–19	1.3–2.2
21 November 2004 ^b	Cloudy with dense fog	12:18–10:23 a.m.	9.9	1.754	3	2	19	Calm air
9 January 2005 ^a	Cloudy with heavy fog	6:30 a.m.–noon	5.5	0.186	5	0	6–11	1.3–1.8
10 January 2005 ^a	Very dense fog with overcast sky	9 January 2005 at 10:35 p.m.–10 January 2005 at 12:40 p.m.	14.1	2.925	7	6	14	1.3–2.2
11 January 2005 ^a	Dense fog with clear to broken clouds	4–8 a.m.	4.0	NA	2	0	18–19	1.3–2.7
15 February 2005 ^a	Fog under a clear sky. Cool night followed by hot to warm day	14 February 2005 at 11:30 p.m.–15 February 2005 at 10:30 a.m.	11.0	0.828	2	0	17	0–2.2
16 February 2005 ^a	Patchy fog with overcast sky	3–10 a.m.	7.0	0.540	0	0	18	2.2
21 February 2006 ^b	Overcast	6:10–11:20 a.m.	5.2	0.544	4	0	9–11	1.7–2.6
22 February 2006 ^b	Cloudy with dense fog	10:50 p.m.–6:10 a.m.	7.7	1.527	7	3	16	0.6–1.8

Data obtained from: <http://cdo.ncdc.noaa.gov/ulcd/ULCD> and http://www.tceq.state.tx.us/cgi-bin/compliance/monops/daily_summary.

^aSamples collected in Baton Rouge.

^bSamples collected in Houston.

Table 2
Comparison of the general characteristics of fogwater collected in Baton Rouge and Houston

Location	Number of samples	pH	TOC (mg CL ⁻¹)	DOC (mg CL ⁻¹)	LWC (g m ⁻³)
Baton Rouge, Louisiana	21	5.0 (2.76–6.37)	6.0 (3.4–13.3)	5.3 (2.4–12.5)	0.084 (0.008–0.33)
Houston, Texas	11	4.3 (3.19–7.19)	11.5 (5.31–15.94)	10.4 (6.3–13.9)	0.065 (0.02–0.126)

Data reported are volume-weighted means, data in parentheses are ranges.

The ionic composition of Houston fog was dominated by sulfate ion (VWM concentration of 953 μN) and ammonium (866 μN). Nitrate concentrations averaged 368 μN . An excess of sulfate and nitrate above ammonium contributes to the more acidic nature of the Houston fog. Significant contributions to Houston fogwater composition were also observed from Na^+ , Cl^- , and Ca^{2+} , suggesting important influences from both sea salt and soil dust. The average nitrate to sulfate ratio was substantially higher in Houston (~ 0.4) than in Baton Rouge (~ 0.1), perhaps reflecting greater contributions from urban/traffic emissions of NO_x . The volume-weighted average concentration of sulfate in Houston was roughly half the sulfate concentration observed in Baton Rouge fog. It is important to recognize that because US sulfur dioxide emissions are dominated by coal-fired power plants, ambient sulfur dioxide and sulfate concentrations are not necessarily higher in larger urban centers. Typical gradients in regional sulfate concentrations measured in this part of the United States (e.g., from the (CASTNET, 2007)) generally show an increase moving eastward.

The chloride to sodium ratio in Baton Rouge fog samples averaged 0.95, while it averaged much higher, 1.68, for the Houston fogwater. The chloride to sodium ratio in sea water is typically approximately 1.16. The lower Cl/Na ratio at Baton Rouge probably reflects acid displacement of HCl from sea salt particles in this polluted environment. Displacement of sea salt chloride occurs due to the uptake of less volatile strong acid such as HNO_3 and H_2SO_4 resulting in release of more volatile HCl. Fog drops that form on these chloride-depleted aerosol particles will also be depleted in chloride relative to sodium, unless the gas phase HCl is also scavenged by the drops. The high deposition velocity of gaseous HCl, however, often means that it is lost fairly quickly from the atmosphere. By contrast, the very high Cl/Na ratio (much higher than the sea water ratio) in Houston fogwater suggests that

other non-sea salt sources of chloride, such as HCl, may be important contributors to Houston fog composition.

3.1. Organic acids

Fig. 3 shows individual contributions of key organic acids to the average DOC present in Baton Rouge and Houston fog samples. Major contributors in Baton Rouge appear to include lactate, pimelate, pyruvate, formate, pinonate, oxalate, acetate, and maleate. In Houston acetic, formic, succinic, pimelic, and maleic acids appear to individually contribute at least 4% of the DOC. Table 4 lists the VWM aqueous concentration (mg CL^{-1}) of selected organic acids quantified in the fog samples.

Lactic acid appears to be a major contributor to the organic carbon in Baton Rouge. Emissions from plant tissues are known to be a source of lactic acid in air (Barker and El Saifi, 1953). The proximity of agricultural farmland near the Baton Rouge sampling site may contribute to higher lactic acid concentrations detected in the fogwater. The average formate-to-acetate ratio in fogwater was approximately 1 in Baton Rouge and approximately 2.2 in Houston. Previous work by several investigators revealed lower formate-to-acetate ratio at sites with higher anthropogenic activity (e.g., Kumar et al., 1993; Srivastava et al., 1993; Tanner and Law, 2003). Kawamura et al. (1985) and Talbot et al. (1988) suggested that the formate-to-acetate ratio can be used as a pollution index. The formate-to-acetate ratio can be higher due to in situ formation of formic acid by photochemical processes and lower due to direct vehicular emissions (Khwaja, 1995; Singh et al., 2006). In contrast to these findings, we see higher formate-to-acetate ratios at our more urban Houston measurement site. This seemingly unusual pattern should be viewed with some caution, however, as only 2 days of fog were collected in Houston and uptake of

Table 3
Comparison of ion concentrations (μN) in fogwater from Baton Rouge and Houston

Location	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Baton Rouge, Louisiana	109.0 (0–396)	6.4 (0–30)	180.8 (3–1068)	1791.4 (0–5775)	114.4 (4–1067)	2077.8 (17–9829)	6.1 (0–80)	26.7 (3–99)	29.9 (7–127)
Houston, Texas	385.8 (49–891)	0.6 (0–6)	368.2 (100–2346)	952.9 (268–3125)	230.2 (35–254)	865.5 (160–2831)	6.5 (0–39)	71.3 (29–144)	251.5 (133–1385)

Data reported are volume-weighted means, data in parentheses are ranges.

these two weak acids into fog drops from the gas phase is pH dependent. The lower pK_a of formic acid renders it more soluble than acetic acid at the lower pH values measured in the Houston fog. Based on the reports by Keene and Galloway (1986), long-range transport of acetic and formic acid is unlikely, hence the acetic and formic acid present is probably of local origin in these regions.

Several organic dicarboxylic acids such as succinic, pimelic, malonic, maleic, and oxalic acids were identified in higher concentrations in Houston than in Baton Rouge (see Table 4). Studies by Kawamura and Kaplan (1987) identified vehicle emissions as possible sources of several organic dicarboxylic acids found in Los Angeles air. Higher concentrations in Houston are consistent with the greater overall mobile source activity in this region and the proximity of Interstate 10, in particular, to the sampling site.

Changes in oxalic acid with time are interesting to evaluate, given past suggestions about aqueous phase oxalate production in clouds and fogs (Ervens et al., 2003; Crahan et al., 2004; Yu et al., 2005). Because changes in fog LWC influence fog solute concentrations through a dilution effect (Möller et al., 1994; Elbert et al., 2000), it is important to normalize for LWC changes with time. In the morning of 21 November 2004 in Baton Rouge, LWC was approximately constant ($\sim 33 \text{ mg m}^{-3}$) from 5 to 6 a.m. During this same time period, the fog concentration of oxalic acid was found to increase from 2.5 to $7 \mu\text{N}$. The oxalic acid concentration continued to climb later in the morning, but these later changes are consistent with a decrease in fog LWC as the fog was evaporating. By contrast, on 10 January 2005, the concentration of oxalic acid in Baton Rouge fogwater remained roughly constant from midnight until 10 a.m. Fog LWC was nearly constant during this event, suggesting that either little oxalic acid was being produced in this fog or that oxalic acid production was roughly balanced by deposition.

3.2. Composition variation with droplet size

Variations in the chemical composition of fog drops as a function of drop size depend on a complex mix of physical and chemical processes. Such variations can exert an important influence on pollution processing by fogs including effects on occult deposition and chemical transformation. We examine the drop size-dependence of several species'

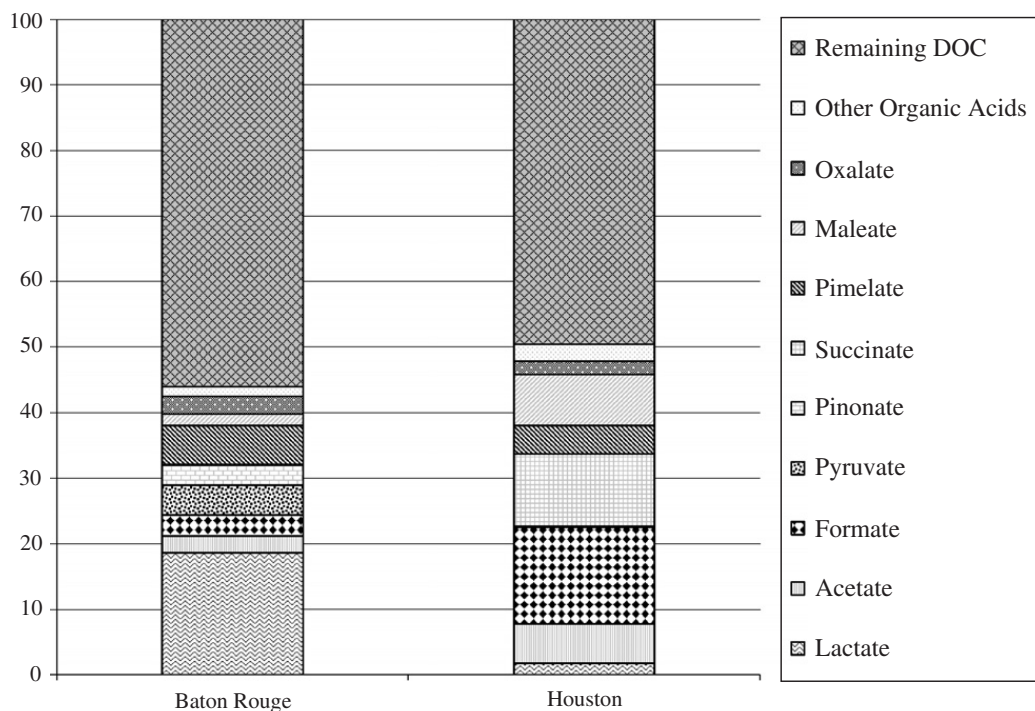


Fig. 3. Average contributions (percent) of measured organic acids to DOC in Houston and Baton Rouge fogwater samples. Other organic acids include butyrate, propionate, methane sulfonate, glutarate, and malonate.

Table 4

Volume-weighted mean aqueous concentrations (mgCL^{-1}) of selected organic acids quantified in fogwater from Baton Rouge and Houston

Location	Lactate	Acetate	Formate	Pyruvate	Pinonate	Succinate	Pimelate	Malonate	Maleate	Oxalate
Baton Rouge	1.31	0.16	0.16	0.07	0.16	0.00	0.01	0.00	0.09	0.08
Houston	0.19	0.64	1.43	0.03	0.00	0.88	0.72	0.20	0.78	0.24

concentrations here, relying in particular on observations from the new three-stage cloud collector. Fig. 4 illustrates the drop size-dependence of pH observed in Houston and Baton Rouge fog samples. The points above the 1:1 line indicates that larger fog drops are less acidic than the smaller fog drops and vice versa. The pH in Houston fog samples revealed that small drops were slightly more acidic than large drops. This pattern has been observed in fogs and clouds from several other environments as well (Munger et al., 1989; Collett et al., 1994). In Baton Rouge fog samples, by contrast, larger drops were typically more acidic than smaller drops.

The drop size-dependent ionic composition of fogwater collected using the three-stage CASCC is shown in Fig. 5 for samples from Houston and Baton Rouge. At both locations sulfate, nitrate, and ammonium were observed to be enriched in smaller

droplets. Similar observations have been reported previously from other locations (e.g., Laj et al., 1998; Collett et al., 1999). K^+ was also strongly enriched in smaller drops at both sites. Concentrations of Na^+ and Mg^{2+} were enriched in larger drops at Houston. The chemical composition of fog droplets is determined by dynamic and complex interactions among a number of processes including nucleation of droplets on a subset of particles that act as CCN, scavenging of other non-activated aerosol particles, uptake of soluble gases, aqueous phase chemical reactions occurring inside the droplets, and dilution of fog solutes by condensational droplet growth. The several roles these processes play in determining how droplet composition varies across the drop size spectrum have been discussed in detail elsewhere (Moore et al., 2004; Ogren et al., 1989). While we lack sufficient

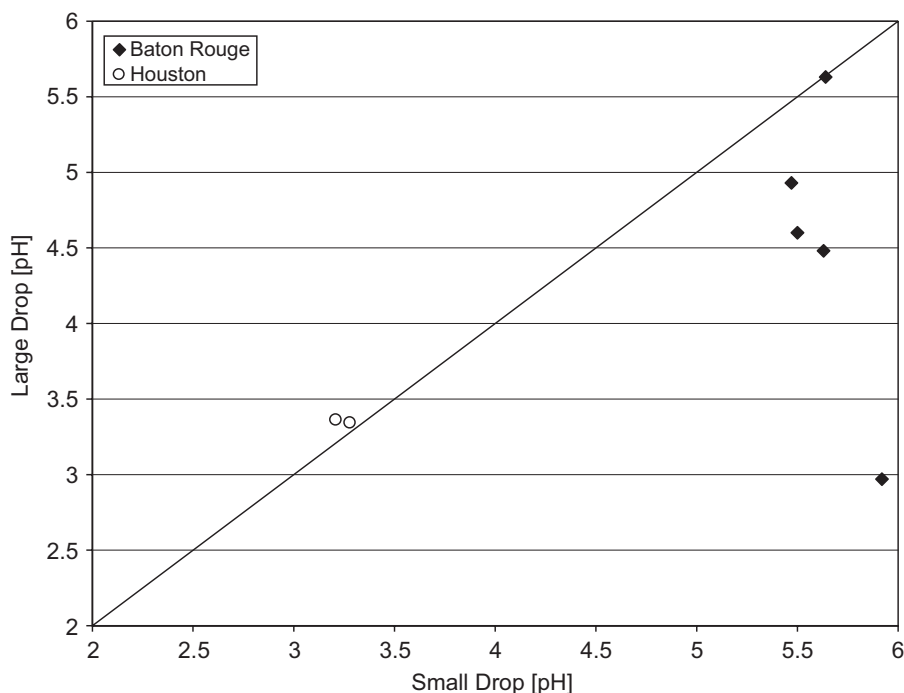


Fig. 4. Drop size-dependent pH in Baton Rouge and Houston fog samples. Samples were collected with an ss-sf-CASCC in Baton Rouge. Houston fog samples reported in this figure were collected with a three-stage CASCC and with an ss-sf-CASCC. Nominal size ranges for small and large drop size fractions for the ss-sf-CASCC are 4–21 μm and $>21 \mu\text{m}$ diameter, respectively, and 4–22 μm and $>22 \mu\text{m}$ for the three-stage CASCC.

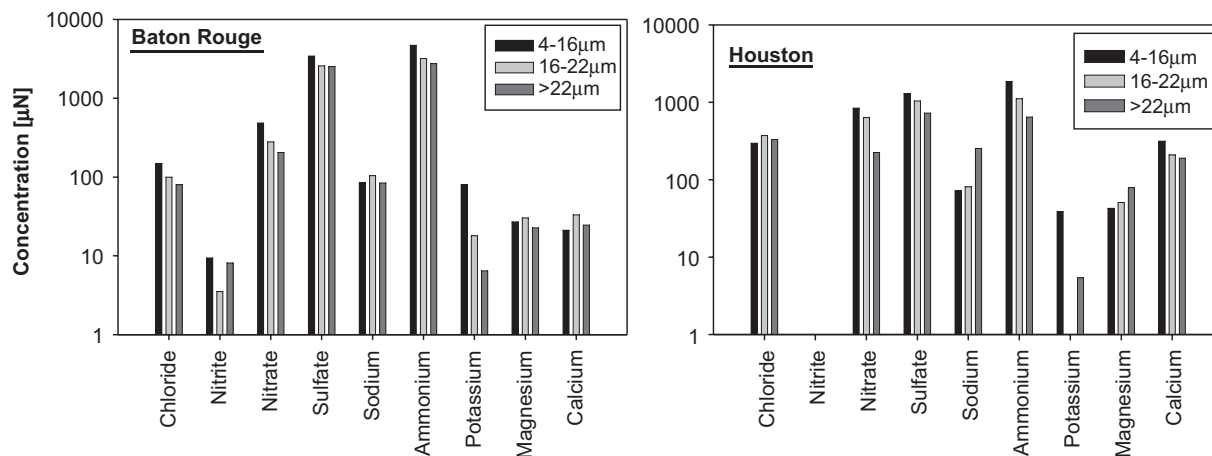


Fig. 5. Variations in ionic composition as a function of fog drop size in Baton Rouge and Houston fogs. Samples were collected with a three-stage CASCC. Size ranges specified are approximate, based on the nominal drop diameter size cuts for the collector.

information to definitively identify all the processes that gave rise to the drop size-dependent composition observed in Houston and Baton Rouge, there are a number of possible hypotheses that can be advanced. For example, the enrichment of sulfate, nitrate, and ammonium in smaller droplets may reflect smaller fog droplet formation on submicron particles of ammonium sulfate and/or ammonium nitrate. The size-dependent composition of aerosol

particles that serve as CCN sometimes leads to a clear pattern of composition vs. drop size in fog droplets; smaller drops are enriched in species associated with smaller particles while larger drops can be enriched in species associated with coarse mode aerosol particles. Non-equilibrium uptake of highly soluble gases can lead to enrichment of some species in smaller drops. Enrichment of nitrate or ammonium in smaller drops, for example, could

reflect preferential uptake of gaseous nitric acid or ammonia by smaller drops where mass transfer is more efficient. In cases where insufficient time is available for the entire fog/gas phase system to achieve phase equilibrium, highly soluble gases like nitric acid can become kinetically “trapped” in smaller droplets. Model simulations of the drop size-dependent composition of radiation fogs in California suggest that this can be an important mechanism contributing to nitrate enrichment in smaller droplets (Hoag et al., 1999). Enrichment of sulfate in smaller drops might also reflect faster uptake and oxidation of sulfur dioxide in these smaller droplets. Reilly et al. (2001) demonstrated how finite rates of mass transport of reactants into large fog drops can sometimes reduce aqueous phase sulfate production relative to rates in smaller fog droplets, especially at higher pH values and in cases where S(IV) oxidation by ozone becomes important.

Fig. 6 shows observed variations of selected organic acid concentrations with drop size in Houston fog. Oxalate was observed to be clearly enriched in small drops, perhaps reflecting its uptake by scavenging of submicron aerosol particles. Formate and acetate were slightly enriched in the medium and smallest drop size classes, respectively. Since formic and acetic acids are expected to enter the drops by uptake from the gas phase, one might expect them to be enriched in higher pH drops. Recall at Houston that only a small pH dependence on drop size was observed, so this is not likely to be a major factor affecting the concentrations of these species. Finite rates of mass transport

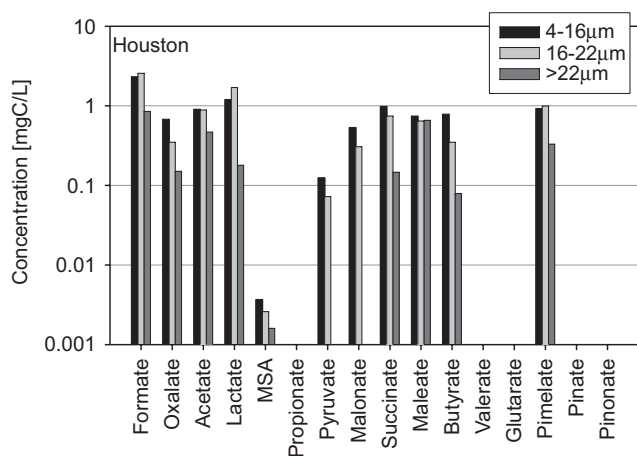


Fig. 6. Variations in organic acid composition as a function of fog drop size for Houston fog. Samples were collected with a three-stage CASC. Size ranges specified are approximate, based on the nominal drop diameter size cuts for the collector.

can, as discussed above, limit attainment of gas–liquid equilibrium for very large drops (e.g., Ervens et al., 2003). We do, in fact, see significantly lower concentrations of both species in the largest drop size class ($D > 22 \mu\text{m}$).

3.3. Composition of carbonaceous materials in Houston and Baton Rouge fogs

Contributions of various measured forms of organic carbon to the total DOC were considered, in order to determine the total fraction of DOC represented by our organic speciation measurements. Fig. 7 shows a breakdown of the fog organic composition for the two sampling sites. Work by several investigators has demonstrated that mono-, di- and poly-functional carboxylic acids are principal contributors to water-soluble organic carbon in fogwater (Gundel et al., 1993; Fachini et al., 1999; Decesari et al., 2000; Herckes et al., 2002a). Consistent with these and other earlier reports, organic acids make up a major fraction, nearly half, of the DOC content in both Baton Rouge and Houston fogs.

Other important contributors (at least 1% of DOC) include carbonyls, amides, and alcohols. Carbonyls comprised 7% and 10% of fog DOC at Houston and Baton Rouge, respectively. The most important carbonyl compounds included formaldehyde, acetaldehyde, and the dicarbonyls glyoxal and methylglyoxal. Smaller concentrations of other carbonyl compounds were also observed, including butanal, pentanal, hexanal, heptanal, octanal, and benzaldehyde. Small DOC contributions were observed from aromatics and alkanes, consistent with our previous findings in California radiation fogs (Herckes et al., 2002b). PAH detected in Houston and Baton Rouge fogs include naphthalene, phenanthrene, 9,10-anthracenedione, and other methyl derivatives of naphthalene. Houston fogwater had a slightly higher contribution of aromatics than Baton Rouge fogwater.

Approximately 42% of the DOC fraction remains unspicated in Baton Rouge fogwater, while 37% is unspicated in Houston fogwater. Several previous studies have suggested that humic-like substances (Zappoli et al., 1999; Gelencsér et al., 2000) may be important contributors to fog composition. We have also observed an abundance of high molecular weight matter in previous studies of California radiation fogs (Herckes et al., 2002a; Collett et al., 2008).

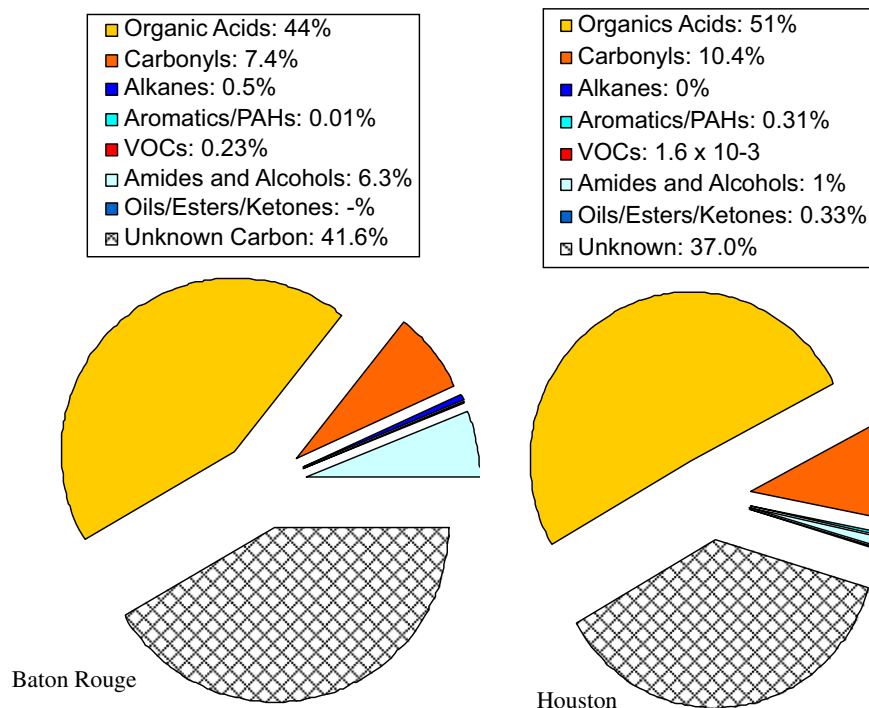


Fig. 7. Average contributions of various organic compound classes to the total dissolved carbon (DOC) contents of Baton Rouge and Houston fogs.

4. Conclusions

Fog samples were collected using single and multi-stage versions of the Caltech active strand cloudwater collector (CASCC) in Baton Rouge, Louisiana and Houston, Texas. Fog pH ranged from strongly acidic to somewhat alkaline in both environments, with minimum and maximum values of 2.6 and 6.4 in Baton Rouge and 3.2 and 7.2 in Houston. The inorganic composition of fog in both locations was dominated by sulfate. The average sulfate:nitrate ratio (equivalents) was nearly 10 in Baton Rouge fogwater and approximately 3 in Houston. The high sulfate content observed in these fogs is similar to fog composition at other eastern US sites and sharply contrasts the nitrate-dominated situation generally observed in fogs from California (Collett et al., 2002).

Fog TOC concentrations in Houston were, on average, nearly twice those in Baton Rouge. Concentrations at both locations were lower than we typically observe in California radiation fogs. Most organic matter in fog samples from both sites was in dissolved form, with only 10–12% in suspended particles removed by sample filtration. Baton Rouge and Houston fog compositions clearly reflect the different environments in which they formed. Houston fogs reflect urban/industrial emis-

sions while Baton Rouge fogs reflect a mix of inputs from urban/industrial, agricultural, and electric power generation activities. For example aromatics and PAH contributed 0.31% of fog DOC in Houston but only 0.01% in Baton Rouge. Organic acids and carbonyls were significant contributors to DOC in both environments.

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