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Jeffrey L. Collett, Jr. and Katherine J. Hoag
Atmospheric Science Department
Colorado State University
Fort Collins, Colorado 80523 USA

and

Spyros N. Pandis
Department of Chemical Engineering
Carnegie Mellon University
Pittsburgh, PA 15213

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EXECUTIVE SUMMARY

The pH values observed in San Joaquin Valley (SJV) fogs typically range between 5.5 and 7.5. Fogwater of this pH supports rapid oxidation of dissolved sulfur dioxide (S(IV)) by ozone. The sulfate produced is nonvolatile. Some of the newly produced sulfate is removed from the air mass via fog drop settling. Another portion is released to the atmosphere as the fog drops evaporate at the end of a fog episode. As S(IV) is oxidized to sulfuric acid, the sulfuric acid deprotonates, releasing hydrogen ions into solution. If not absorbed by another species in solution, the hydrogen ions cause the drop pH to decline rapidly. This drop in pH slows the ozone pathway for S(IV) oxidation.

Previous, preliminary tests of SJV fog samples revealed that they often possessed a significant ability to neutralize added acid. As sulfuric acid was added to these samples their pH declined much less than expected. This observation suggested that the pH of these fogs could remain elevated longer than previously expected, thereby supporting rapid rates of sulfate production for a much longer period of time.

Although the idea of internal buffering of added acids was not new, the amount of buffering exhibited by these samples was larger than could be readily explained by the availability of known weak acids and bases (including ammonia, bicarbonate, acetate and formate) in solution. Accordingly, an effort was undertaken to more fully characterize the buffering of SJV fog samples, including those collected during the 1995 Integrated Monitoring Study (IMS95) and to examine its effects on fog chemistry and aerosol formation rates.

APPROACH

In order to better understand the magnitude of the observed buffering, its temporal and spatial variations, its cause and its effects on aqueous aerosol formation, Colorado State University (CSU) and Carnegie Mellon University (CMU) conducted a joint investigation of this

phenomenon. CSU's efforts focused on better characterizing the observed buffering and identifying key parameters needed to include the unknown buffering agent in a fog chemistry model. CMU incorporated this formulation into their radiation fog model and examined the effects of the additional buffering on aerosol production rates and temporal changes in droplet pH.

In order to better characterize the buffering, CSU performed acid titrations on additional fog samples using a new, automated titrator. Several investigations were conducted to characterize buffering agents present in the fog. Measurements were made of bicarbonate, acetate, and formate concentrations in a subset of the titrated fog samples. These results were combined with previous measurements of ammonium to determine what portion of the observed buffering was due to these known species. Titrations were performed on pairs of filtered and unfiltered fog sample aliquots to determine if the buffering observed was associated with undissolved or dissolved material.

Based on results from these investigations, some candidate buffering agents were identified. A composite SJV fog sample was submitted for GC-MS analysis of substituted phenols, several of which are capable of acid buffering in the pH range of interest (4-7). CSU also communicated with the U.S. Geological Survey in Denver regarding analysis of humic acids, another candidate buffering compound.

Results from the buffering measurements were provided to CMU for use in model simulations. Using this information, CMU modified their radiation fog model to include the observed buffering and examined the effect of this buffering on the fog pH in a simulation of an IMS95 Bakersfield fog episode. The model was also used to examine effects of the buffering on sulfate, nitrate, and ammonium concentrations.

MAJOR CONCLUSIONS

The analysis of acid buffering in SJV fogs has produced a number of significant findings and recommendations:

- Concentrations of ammonia, bicarbonate, acetate, and formate in fog samples were sufficient to explain nearly all measured buffering in rural fogs from the Kern Wildlife Refuge site. Concentrations of these species were not capable of explaining the measured buffering in urban fogs from Bakersfield and Fresno.
- Significant, unexplained acid buffering was observed in most Bakersfield and Fresno fog samples. The buffering occurred over a broad pH range from approximately pH 4 to 7.
- Previous analysis of IMS95 fog data revealed that organic species concentrations were generally enriched in urban fogs, while concentrations of major ions like nitrate, sulfate, and ammonium typically didn't vary much between urban and rural fogs. This suggests that the unexplained buffering may be associated with organic solutes.
- The unexplained buffering in the fog samples was found to correlate very well with measured low molecular weight organic species (acetate, formate, and formaldehyde) concentrations. For example, the correlation between unexplained buffering and the sum of formate and acetate concentrations was quite strong ($r^2 = 0.96$). Analysis showed that neither acetate nor formate was directly responsible for the buffering. The strong correlation, therefore, suggests that other species that are strongly correlated with acetate, formate, and formaldehyde (perhaps higher molecular weight organic compounds of urban origin) are probably responsible for the unexplained buffering. Only modest correlations were found between the amount of unexplained buffering and inorganic ion concentrations.
- Filtration tests revealed that the buffering was associated entirely with dissolved material, rather than undissolved particulate matter.
- GC-MS analysis of substituted phenols revealed that, while several of these compounds were present in the fogwater, their concentrations were too low to account for any significant fraction of the observed buffering.

- Humic acids were identified as candidate compounds for the unexplained buffering, since they can be incorporated into fog drops via particle scavenging and exhibit buffering in the pH range of interest. Although characterization of humic materials in fogwater is possible, this would require processing of many liters of fogwater. This volume of SJV fogwater is currently not available.

- A method was found to include the additional, unexplained fog sample buffering in the CMU fog model used to simulate IMS95 fog episodes. Because the buffering occurred over a broad pH range, it was not possible to satisfactorily simulate it in the model by adding a few, hypothetical buffering agents. Instead, an empirical buffering function was formulated and included in the electroneutrality equation solved by the model. This method yielded good agreement between the observed and model-simulated buffering.

- Simulations of the effect of the additional buffering in the December 10, 1995 fog episode at Bakersfield revealed a significant impact on the fog chemistry. The additional buffering permitted the fog pH to remain 0.3-0.7 pH units higher than predicted in a simulation without the additional buffering. As a result the rate of S(IV) oxidation by ozone was significantly enhanced, leading to an increase in sulfate aerosol present following the fog episode of approximately 50%. The buffering had no effect on nitrate concentrations and only modest (~10%) effects on ammonium concentrations.

- The effects of the buffering on sulfate production are very sensitive to ambient ozone concentrations. Even changes in ozone concentration as low as 0.5 ppb can significantly alter the amount of aqueous sulfate production predicted by the model.

- While measured ozone concentrations during IMS95 fog episodes were typically a few ppb, model simulations suggest the ozone should be consumed at night by reaction with NO. Given the sensitivity of the sulfate production to ozone concentrations, it is strongly recommended that future studies of aerosol processing by fogs in the SJV carefully evaluate the accuracy of ozone measurements at levels below 5 ppb.

- Since the unexplained buffering in the fog appears capable of substantially increasing post-fog aerosol sulfate levels, it is recommended that this issue continue to be investigated in future fog campaigns in the SJV. It is recommended that sample titrations be performed in

the field and that they be accompanied by measurements of ambient carbon dioxide concentrations. It is also recommended that significantly larger volumes of fogwater be collected for analysis of organic solutes present in the fog drops. Future studies of the buffering should be accompanied by further model simulations to facilitate understanding the impact of the buffering on aerosol processing.

1. Introduction

The existence of effective aqueous oxidants in the atmosphere permits the rapid oxidation of dissolved sulfur dioxide in clouds and fogs. S(IV) can be oxidized in cloud or fog drops by several pathways. Important oxidants include H_2O_2, O_3 and O_2 (catalyzed by trace metals). The cloud or fog drop pH is an important determinant of the relative rates of the various oxidation pathways (Seinfeld, 1986). The rate of oxidation by H_2O_2 is independent of pH (in the pH range found in atmospheric cloud and fog drops) and is typically the fastest oxidation pathway at low pH. Rates of S(IV) oxidation by O_3 and O_2 (catalyzed by Fe(III) and Mn(II)) increase with cloud or fog drop pH and can be important at higher pH (typically >5) or in the absence of significant H_2O_2

In analyzing fog events sampled during the 1995 Integrated Monitoring Study (IMS95), we have determined that S(IV) oxidation by ozone is often the dominant aqueous phase sulfate production pathway. This occurs because the fog pH generally is close to neutral, with samples from the study exhibiting a median pH of 6.49. As S(IV) is oxidized sulfuric acid is produced leading to acidification of the fog drops. In the absence of any acid buffering, the droplet pH can decline rapidly. Drop acidification quickly depresses S(IV) oxidation by ozone and can also significantly alter rates of trace metal catalyzed S(IV) autooxidation.

One mechanism counteracting the tendency for droplets to acidify is uptake of gaseous ammonia, in those environments, including the San Joaquin Valley (SJV), where excess ammonia exists in the gas phase. This is a well recognized phenomenon which has been included in many model studies of aqueous phase sulfate production. Less well recognized is the possibility that a significant acid buffering capacity can exist within the droplets themselves. Jacob et al. (1986) considered fogwater alkalinity, which they defined as the deficiency of aqueous phase H^+ with respect to the reference system of neutralized fogwater species and calculated as

$$[ALK] = [HCOO^-] + [CH_3COO^-] + [CH_3CH_2COO^-] + [CH_3CH(OH)COO^-] + [HCO_3^-] \quad (1)$$
$$+ [NH_3(aq)] + [OH^-] - [H^+]$$

Facchini et al. (1992) have also examined fogwater acidity (equivalent to negative alkalinity) while Liljestrand (1985) has considered acid buffering associated with proton exchange in solution and uptake of soluble gases. In all of these cases, the species considered have been mainly restricted to the NH_3-HNO_3-H_2SO_4 system, with addition of soil dust and sea salt components, the carbonate system, low molecular weight organic acids, and S(IV)-aldehyde complexes.

Despite the appeal of modeling cloud and fogwater as a relatively simple system, there is increasing evidence that its composition may be much more complex than is typically considered. Organic compounds, for example, appear to contribute significantly to atmospheric water drop compositions in many environments (Leuenberger et al., 1988; Munger et al., 1989; Capel et al., 1990; Tremp, 1992). IMS95 fog samples were found to possess significant amounts of total organic carbon (TOC = 5-41 ppmC), with the fraction of TOC accounted for by measured concentrations of formaldehyde and C_1-C_3 carboxylic acids averaging only 19% (Collett et al., 1998). Erel et al. (1993) similarly reported that only 20% of the TOC in SJV fogwater collected at Bakersfield was comprised of formaldehyde, formate and acetate.

Acid titrations conducted in the field and in our laboratory of more than one hundred SJV fog samples collected from several locations in 1994-96 revealed that SJV fogwater often possesses a significant internal acid buffering capacity. In order to determine whether the observed buffering capacity could be explained by the presence of traditionally considered fogwater solutes and to characterize possible sources of any unexplained buffering capacity, we undertook a more detailed study of the buffering present in a subset of SJV fog samples. These findings are presented here, along with a numerical model analysis of the effects of the observed buffering on aerosol processing by SJV fogs, including changes in aqueous phase sulfur oxidation.

2. Experimental Measurements of Buffering in SJV Fog Samples

Fogwater collected at Bakersfield in January 1994 has been titrated numerous times between one and four years after collection. All the IMS95 samples that still had sufficient sample volume were titrated in August 1997. A few IMS95 samples had originally been titrated in the field at the time of collection; some were also titrated in June 1996. The following section describes the methods and results of these titrations.

Previous to 1997 all the titrations performed on the fog samples were done manually. Several kinds of electrodes were used, including an Orion semi-micro combination pH electrode and a Microelectrodes, Inc. MI-710 combination pH electrode. Orion 250 or 290 pH meters were used and the electrode response was calibrated using pH 4.01 and 7.00 buffers. Occasionally a calibration point at 10.01 was also used. A sample volume of 1.0 mL of fog was used in a 2.0 ml cryovial. An initial pH of the sample was taken and then 1, 2 or 10 mN H_2SO_4 was added in 10 µL increments, mixing and measuring the pH after each addition. Duplicates using this method were performed and the results were very repeatable (see Figure 2.1 for example data).

Fog samples were titrated for this study using a QC-Titrate automated titration system from Man-Tech Associates, Inc., in conjunction with a Microelectrodes, Inc. MI-410 combination pH electrode. A three point electrode calibration (pH 4.01, 7.00, and 10.01) was used. Sample volumes of 1.0-1.5 ml were used for the titrations. Potentiometric titrations were performed with the auto-titrator using 10 mN sulfuric acid. The increment of acid added was controlled by selecting a maximum allowable pH change of 0.25 pH units between injections. The smallest volume of titrant possible to add is one microliter, giving very good resolution of the shape of the titration curve. Titrations were performed with stirring in open glass reaction vials. No temperature control was used. Titration durations varied, but were typically a few minutes. Fog sample dilutions resulting from titrant addition were accounted for when interpreting titration results. Maximum dilutions were typically of the order of 5-10%. Duplicates were performed and were found to be very repeatable (see Figure 2.2).

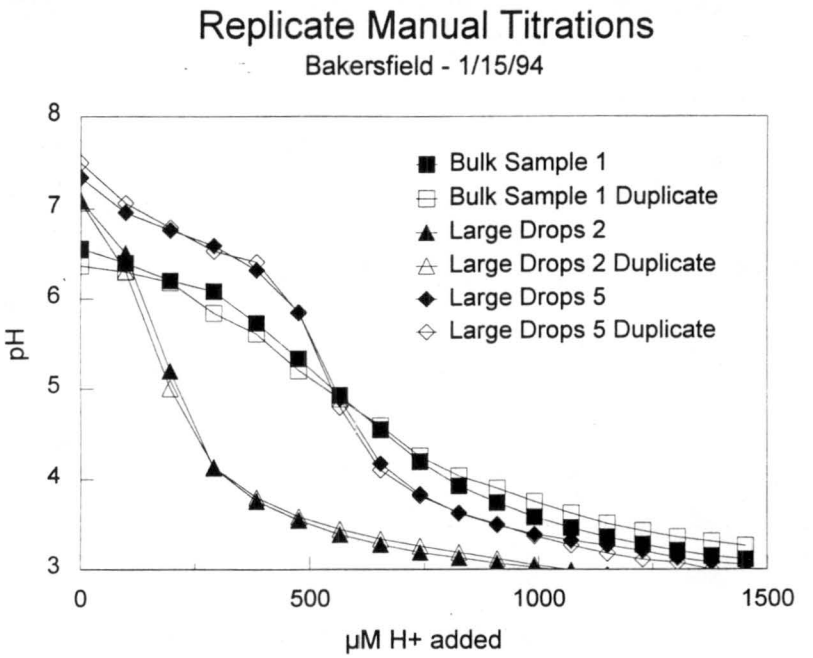

Figure 2.1. Replicate manual titrations of 1994 Bakersfield fog samples

Base titrations were also performed on selected samples. For these titrations, 20 μL of 0.1 N H_2SO_4 were added to 2 ml of sample to acidify the sample before pipetting 1.5 ml into the titration vial. Then automatic base titrations were performed in a manner similar to the acid titrations using 10 mN KOH.

As a control check for each method, a daily titration of nanopure water (water purified sequentially by reverse osmosis followed by ion exchange using a Barnstead Nanopure system) was performed in the same manner as for the samples. These checks revealed that the method was working properly before the titrations were started each time and that interaction of the titrated sample with air in the laboratory did not contribute significant buffering capacity to the sample during the titration. The titrations reported here were completed in August 1997, using "extra" fogwater stored in refrigerated polyethylene bottles.

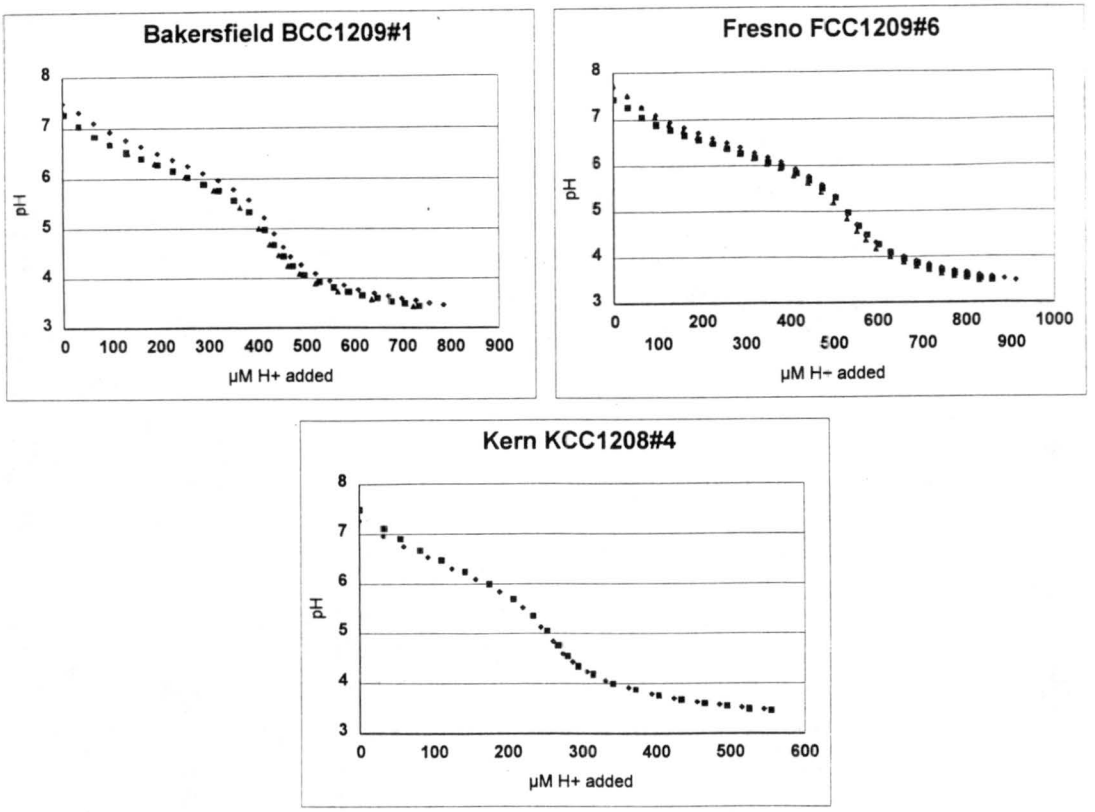

Figure 2.2. Replicate automatic titrations of IMS95 samples.

Table 2.1 shows when each sample was titrated for each of the investigations described below. Automatic titrations are denoted with an (A). A comparison of the manual and automatic titration methods was performed to permit comparison of the recent results to data collected in previous years. Eight samples were selected for this intercomparison study from 1994 Bakersfield samples and IMS95 samples from Bakersfield, Fresno, and Kern Wildlife Refuge. In most cases, manual and automatic titrations performed within a week of each other were very close with minor deviations in some cases. Figure 2.3 illustrates a comparison of the manual and automated titration curves obtained for an IMS95 fog sample from Bakersfield.

Table 2.1. Sample Titration Record

Site	Sample Name	Field Titration	------- Manual titrations -------			Manual/Auto Comparison	Acid titrations	Filtered	Titrated same day as HCO3- Measurement	Base titration
BAK 1/15/94	SM C ASCC 1		6/5/96	06/06/96	06/07/96			8/18/97(A)	08/27/97 (A)	9/3/97 (A)
	SM CASCC 1B		6/5/96	06/06/96						
	SM CASCC 2		6/5/96	06/06/96	06/07/96			8/18/97(A)	08/27/97 (A)	
	Sm CASCC 3									
	LG LG 1		05/08/95	06/07/96	07/31/97	8/7/97 (A)			08/27/97 (A)	
	Lg Lg 1b									
	LG LG 2		05/08/95	06/07/96					08/27/97 (A)	
	Lg Lg 2B									
	Lg Lg 3									
	LG SM 1		06/07/96							
	LG SM 2		05/08/95	06/06/96					08/27/97 (A)	
BKA 1995	BCC1209#1						8/12/97 (A)	8/15/97 (A)	8/27/97(A)	9/3/97 (A)
	BCC1209#2						8/12/97 (A)	8/15/97 (A)		
	BCC1209#3						8/12/97 (A)			
	BCC1209#4						8/12/97 (A)	8/15/97 (A)		
	BCC1210#1		08/01/97			8/7/97 (A)	8/12/97 (A)	8/15/97 (A)		
	BCC1210#2	12/22/95					8/12/97 (A)			
	BCC1210#3	12/22/95					8/12/97 (A)			
	BCC1210#4	12/22/95	08/01/97			8/7/97 (A)	8/12/97 (A)			
	BCC1210#5	12/22/95					8/12/97 (A)			
	BCC1210#6	12/22/95					8/12/97 (A)			
	BCC1210#7	12/22/95					8/12/97 (A)			
	BCC1210#8	12/22/95					8/12/97 (A)			
	BCC1218#1	12/22/95					8/12/97 (A)			
KERN 1995	KCC1208#2						8/13/97 (A)	8/18/97 (A)	8/27/97 (A)	
	KCC1208#3						8/13/97 (A)			
	KCC1208#4						8/13/97 (A)	8/18/97 (A)		9/3/97 (A)
	KCC1208#5						8/13/97 (A)			
	KCC1208#6						8/13/97 (A)			
	KCC1208#7						8/13/97 (A)			
	KCC1209#1						8/13/97 (A)			
	KCC1209#2						8/13/97 (A)			
	KCC1209#3						8/13/97 (A)			
	KCC1209#4						8/13/97 (A)			
	KCC1209#5						8/13/97 (A)			
	KCC1209#6						8/13/97 (A)			
	KCC1214#2						8/13/97 (A)			
	KCC1214#3						8/13/97 (A)			
	KCC1214#4						8/13/97 (A)	8/18/97 (A)		
	KCC1218#1						8/13/97 (A)			
	KCC0101#1	01/02/96					8/13/97 (A)			
	KCC0101#2						8/13/97 (A)			
	KCC0101#3						8/13/97 (A)			
	KCC0102#1						8/13/97 (A)			
	KCC0102#2						8/13/97 (A)			
	KCL1208#3						8/13/97 (A)			
	KCL1208#5						8/13/97 (A)			
	KCL1208#7						8/13/97 (A)			
	KCL1208#9						8/13/97 (A)			
	KCL1208#11						8/13/97 (A)			
	KCL1208#13						8/13/97 (A)			
	KCS1208#2						8/13/97 (A)			
	KCS1208#4						8/13/97 (A)			
	KCS1208#6						8/13/97 (A)			
	KCS1208#10						8/13/97 (A)			
	KCS1208#12						8/13/97 (A)			

Table 2.1. Sample Titration Record (Continued)

Site	Sample Name	Field Titration	------- Manual titrations -------			Manual/Auto Comparison	Acid titrations	Filtered	Titrated same day as HCO3- Measurement	Base titration
KERN1995	KCL1209#1		06/08/96	08/01/97		8/7/97 (A)	8/14/97 (A)			
	KCL1209#2		06/08/96				8/14/97 (A)			
	KCL1209#3		06/08/96				8/14/97 (A)			
	KCL1209#4		06/08/96	08/01/97	08/07/97	8/7/97 (A)	8/14/97 (A)			
	KCL1209#5		06/08/96				8/14/97 (A)			
	KCL1209#6						8/14/97 (A)			
	KCS1209#1		06/08/96							
	KCS1209#2		06/08/96				8/14/97 (A)			
	KCS1209#3		06/08/96				8/14/97 (A)			
	KCS1209#4		06/08/96				8/14/97 (A)			
	KCS1209#5		06/08/96				8/14/97 (A)			
	KCS1209#6						8/14/97 (A)			
	KCL1214#2						8/14/97 (A)			
	KCL1214#3						8/14/97 (A)			
	KCL1214#4						8/14/97 (A)			
	KCS1214#3						8/14/97 (A)			
	KCS1214#4						8/14/97 (A)			
	KCL0101#1						8/14/97 (A)			
	KCL0101#2	01/02/96					8/14/97 (A)			
	KCL0101#3						8/14/97 (A)			
	KCS0101#1						8/14/97 (A)			
	KCS0101#2	01/02/96					8/14/97 (A)			
	KCL0102#1						8/14/97 (A)			
	KCL0102#2						8/14/97 (A)			
	KCS0102#1						8/14/97 (A)			
	KCS0102#2						8/14/97 (A)			
	KIL1208#3						8/13/97 (A)			
	KIM1208#3						8/13/97 (A)			
	KIS1208#3						8/13/97 (A)			
FSF 1995	FCC1208#1						8/11/97 (A)	08/15/97 (A)		9/3/97 (A)
	FCC1208#2						8/11/97 (A)			
	FCC1208#3						8/11/97 (A)			
	FCC1208#4						8/11/97 (A)			
	FCC1208#5						8/11/97 (A)			
	FCC1208#6						8/11/97 (A)			
	FCC1208#7						8/11/97 (A)			
	FCC1208#8						8/11/97 (A)			
	FCC1209#1						8/11/97 (A)			
	FCC1209#2						8/11/97 (A)			
	FCC1209#3						8/11/97 (A)			
	FCC1209#4						8/11/97 (A)			
	FCC1209#5						8/11/97 (A)			
	FCC1209#6						8/11/97 (A)	08/15/97 (A)	8/27/97 (A)	
	FCC1231#1	01/01/96	08/01/97			8/7/97 (A)				
	FCC1231#2						8/11/97 (A)	08/15/97 (A)		
	FCC1231#3	01/01/96	08/11/97				8/11/97 (A)			
	FCC1231#4						8/11/97 (A)			
	FCC0103#1						8/11/97 (A)			
	FCC0103#2	01/04/96	08/07/97	08/11/97		8/7/97 (A)	8/11/97 (A)			
	FCC0103#3						8/11/97 (A)			
TOWER 96	GCC0112#1						8/12/97 (A)			
	MCC0112#1						8/12/97 (A)			
	MCC0112#2						8/12/97 (A)			
	MCC0112#3						8/12/97 (A)			
	MCC0112#4						8/12/97 (A)			
	TCC0112#1						8/12/97 (A)			
	TCC0112#2						8/12/97 (A)			
	TCC0112#3						8/12/97 (A)			
	TCC0112#4						8/12/97 (A)			
	MCC0114#1						8/13/97 (A)			
	MCC0114#2						8/13/97 (A)			
	MCC0114#3						8/13/97 (A)			
	TCC0114#1						8/13/97 (A)			
	TCC0114#2						8/13/97 (A)			
	TCC0114#3						8/13/97 (A)			

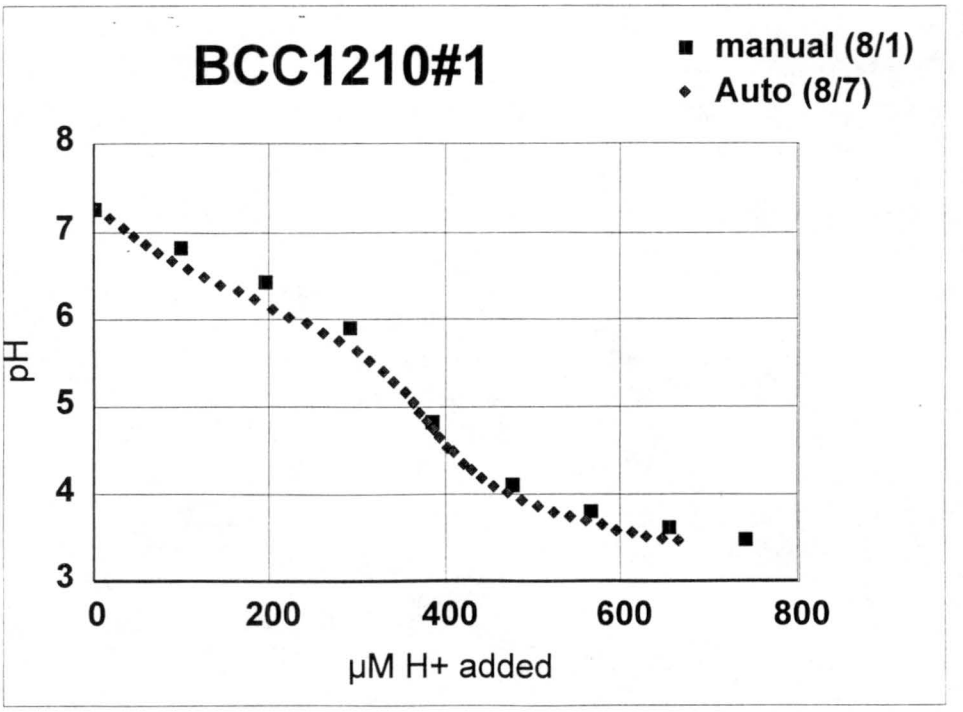

Figure 2.3. Comparisons of manual and automated titration curves for the first fog sample collected at Bakersfield on 12/10/95.

Detailed buffering analyses on selected fog samples

More than 100 fog samples from the IMS95 and previous SJV fog studies were titrated. These titrations typically revealed the presence of significant internal buffering in the fog. In order to determine whether the observed buffering could be accounted for by traditionally considered species (e.g., bicarbonate, ammonia, acetate, and formate), and to better characterize any unexplained buffering, a subset of 11 samples was selected for further, detailed consideration. In order to avoid confusion, these samples will be referred to henceforth as the 11 special study samples. The selected special study samples included some from each of the three IMS95 sampling sites as well as some collected during a highly polluted fog event sampled in Bakersfield in 1994. These samples are listed in Table 2.2, along with their collection date and pH values measured in the field and at the time of laboratory titration. Collection dates range from January 1994 to January 1996. Automated titrations reported in this work were conducted

in August 1997, although earlier, manual titrations had been conducted on a number of the special study samples as well.

Table 2.2. Titration special study sample characteristics

Sample Name	Sample Date	Field pH	Initial PH*	Unexpl. Buffer-ing** µM	HCO_3^-*** µN	NH_4^+ µN	NO_3^- µN	SO_4^{2-} µN	$HCOO^-$ µN	CH_3COO^- µN	HCHO µM
Bakersfield											
BAK011594#1	1/15/94	6.03	7.39	240	264	7452	3731	520	NA****	NA	NA
BAK011594#2	1/15/94	6.58	7.27	246	204	3964	2069	259	NA	NA	NA
BCC1209#1	12/9/95	7.04	7.34	83	358	937	332	136	76	117	46
BCC1209#2	12/9/95	7.02	7.37	76	284	945	371	221	63	113	53
BCC1209#4	12/9/95	6.92	7.3	129	353	1233	474	158	123	224	71
BCC1210#1	12/10/95	6.32	7.22	142	254	1168	328	160	85	380	135
Kern Wildlife Refuge											
KCC1208#4	12/9/95	6.8	7.5	31	237	546	248	41	28	47	23
KCC1214#4	12/15/95	7.43	7.23	27	240	566	292	39	NA	NA	13
Fresno											
FCC1208#1	12/9/95	5.89	7	146	259	1220	452	142	84	369	76
FCC1209#6	12/10/95	6.38	7.75	60	464	1225	396	80	NA	NA	NA
FCC1231#2	1/1/96	6	7.18	126	196	994	352	118	NA	NA	NA

* Initial titration pH for titrations conducted in 8/97
** Extra H^+ required to protonate unknown buffering agents while titrating from initial pH to pH 5
*** HCO_3^- concentrations were measured on 8/27/98; other species were measured several weeks following sample collection
**** Concentration not available

In order to better interpret observed acid buffering in the 11 special study fog samples, their bicarbonate concentrations were measured in August 1997 by ion chromatography. The measured samples were taken from the same refrigerated polyethylene storage bottles from which the August 1997 titration samples were taken. A gradient NaOH elution method was used to separate ionic components on a Dionex AS-11 ion exchange column for conductivity detection. Bicarbonate standards were prepared immediately before the start of the analysis due to the potential for CO_2 gas exchange during storage. This method was also used to quantify concentrations of C_1-C_3 carboxylic acids (formate, acetate, propionate, pyruvate, and oxalate) in the fog samples. Carboxylic acid determinations were made both on field aliquots of the samples

(preserved by addition of a small amount of chloroform to kill microorganisms in the sample) and on the unpreserved fog samples used for the acid titrations and the bicarbonate analysis.

Several additional tests were performed to further characterize possible sources of buffering:

- To determine whether particulate matter in the samples contributed any significant buffering to the collected fogwater, filtered and non-filtered sample aliquots of the 11 special study samples were titrated concurrently in August 1997. A 0.2 μm pore size Anotop10 IC inorganic membrane filter (10 mm diameter) was used with a 3 cc syringe to filter 2 ml of fog sample into a cryovial before pipetting 1.5 ml of filtered sample into a titration vial. Filtered and unfiltered samples were titrated as described above. Filtered and unfiltered titrations of deionized water showed that the filtering process did not contribute to the buffering capacity of the liquid.
- A sample of SJV fogwater exhibiting significant acid buffering was analyzed for phenols (4-chloro-3-methylphenol, 2-cholorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 4,6-dinitro2mephenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, phenol, and 2,4,6-trichlorophenol were measured by EPA Method 604, Spectrum Laboratories, Inc., Fort Lauderdale, Florida) by GC-MS in October 1997. In order to provide useful detection limits a 1 liter sample of fog was required for analysis. Meeting this requirement necessitated preparing a composite sample made up of remaining portions of several highly buffered SJV fog samples from the 1994 Bakersfield study and from IMS95. The fogwater used in the composite came from the same "extra" fogwater samples stored in refrigerated polyethylene bottles that were used in the titrations. As discussed below, evidence from other investigations suggested phenolic compounds could contribute to acid buffering in SJV fogs.
- Spectroscopic scans were performed on three filtered and unfiltered samples to measure light absorbance by fog samples over a wavelength range from 270 nm to 1100 nm. Observations made in the field indicated that collected fog samples were often dark in color with a frequent yellow cast, particularly at the Fresno site.

Buffering Observations

Without measurements of known buffering species (e.g., formate, acetate and conjugate bases of other C_1-C_3 carboxylic acids, carbonate/bicarbonate and ammonia) it is difficult to evaluate whether these species are capable of explaining all the buffering observed in a particular fog sample. Measurements of ammonium made in the samples were used together with sample pH and temperature to determine aqueous ammonia concentrations from equilibrium considerations. August 1997 measurements of C_1-C_3 carboxylic acids (formic, acetic, pyruvic, propionic and oxalic acids) in the samples used for the titrations revealed that these species were either not detectable or present only at trace levels. Although in contrast to our earlier 1996 measurements of significant concentrations of formic and acetic acids in preserved (chloroform was added as a biocide) IMS95 fog samples (Collett et al., 1999), the absence of these species in the unpreserved fog sample aliquots used for the titrations was expected. The absence of these species in the titrated samples poses no problem for this work and actually simplifies the task of determining whether remaining buffering can be explained on the basis of ammonia and bicarbonate concentrations. Of course the presence of low molecular weight carboxylic acids in the fog at the time of sampling can potentially influence the fog's pH evolution. In practice, however, this effect is small in SJV fogs because the fog pH typically remains high (> 6) relative to the pKa's of formic and acetic acids (approximately 3.7 and 4.8, respectively).

One result of the loss of low molecular weight carboxylic acids from the stored samples is that the stored sample pH typically rises. This change, which normally occurs over a period of several days following sample collection, is reflected in Table 2.2 where the sample pH measured immediately after collection in the field and the stored sample pH measured in August 1997 are both listed for each of the 11 special study samples. The increase in sample pH, the refrigeration of the stored samples, and their storage in an indoor environment can all affect the concentrations of bicarbonate, carbonate, and dissolved carbon dioxide in the samples. Rising sample pH, sample cooling, and the higher concentrations of carbon dioxide found in indoor environments are all expected to lead to increases in the concentrations of inorganic carbon species in stored samples.

Bicarbonate concentrations measured in the 11 special study fog samples in August 1997 ranged from 43 to 464 μM (see Table 2.2). Analysis of these bicarbonate concentrations and the field fog pH and atmospheric temperature revealed that the fog samples often contained much higher bicarbonate concentrations than expected from equilibrium with typical atmospheric carbon dioxide concentrations (carbon dioxide was not measured during the study). Equilibrium calculations using the stored sample pH and temperature (277 K), however, reveal that the measured bicarbonate concentrations are consistent with sample storage in an environment containing several hundred ppmv of carbon dioxide, a typical indoor range. The samples were not found to be in equilibrium with a single gas phase carbon dioxide concentration (the predicted equilibrium carbon dioxide concentration decreased with increasing sample pH suggesting that higher pH samples had not yet attained equilibrium with the indoor storage area carbon dioxide concentration), necessitating measurement of bicarbonate levels in individual samples.

The bicarbonate concentrations, together with previously measured ammonium concentrations and sample pH were used to construct theoretical buffering curves for several fog samples. These curves were then compared to measured buffering curves, constructed from acid titration data, to evaluate whether all buffering in the samples was accounted for. Formate and acetate were not included in the theoretical curves because, as mentioned above, no significant concentrations of these species were observed in the bicarbonate analysis chromatograms (the same method can be used to quantify formate and acetate) at the time of the titrations. In order to present these findings some further definitions are first required.

The amount of buffering can be expressed in terms of buffering intensity β, given by the equation:

$$\beta = -\frac{dC}{dpH} \tag{2}$$

for an acid titration of a basic sample and

$$\beta = \frac{dC}{dpH} \tag{3}$$

for a base titration of an acidified sample, where C is the amount of added titrant.

Analyzing a curve of buffering intensity, β, as a function of pH, one should see relative maxima when the pH value equals the pKa of the responsible buffering agents. This occurs because the change in pH is expected to be small for a given acid addition when the solution pH is equal to the buffer's pKa. In the case of dissolved carbon dioxide, we expect to see a strong buffering contribution near its first pKa of 6.4 (dissociation to form bicarbonate). The pKa for deprotonation of ammonium (9.2) is much higher; therefore, we see a contribution to buffering from ammonium formation at high pH. Water itself is well-buffered at high and low pH, since in these ranges a significant change in pH can only be achieved by addition of a large amount of acid or base. These features are illustrated in Figure 2.4, which depicts theoretical buffer intensity curves for a pure water sample, dissolved carbon dioxide (present as carbonic acid, bicarbonate and carbonate), dissolved ammonia (present as ammonia and ammonium), and a water sample containing both dissolved carbon dioxide and ammonia. Note how the buffering from each individual species yields a peak in the overall buffer intensity curve at the species' pKa.

Figure 2.5 illustrates the theoretical buffering intensity curves for two samples collected at the Kern Wildlife Refuge (KWR) site. In both cases the buffering from bicarbonate is evidenced from the buffering intensity peak at 6.4. The theoretical and measured buffering curves are quite close to one another, so that the difference curve is very close to zero (because the curves are so steep below pH 4, the difference curve becomes a lot noisier there; this is unimportant for our purposes since we are most interested in buffering against acidification in the high pH range). This result implies that the buffering in the sample is nearly accounted for by species normally considered as important buffers in the fog.

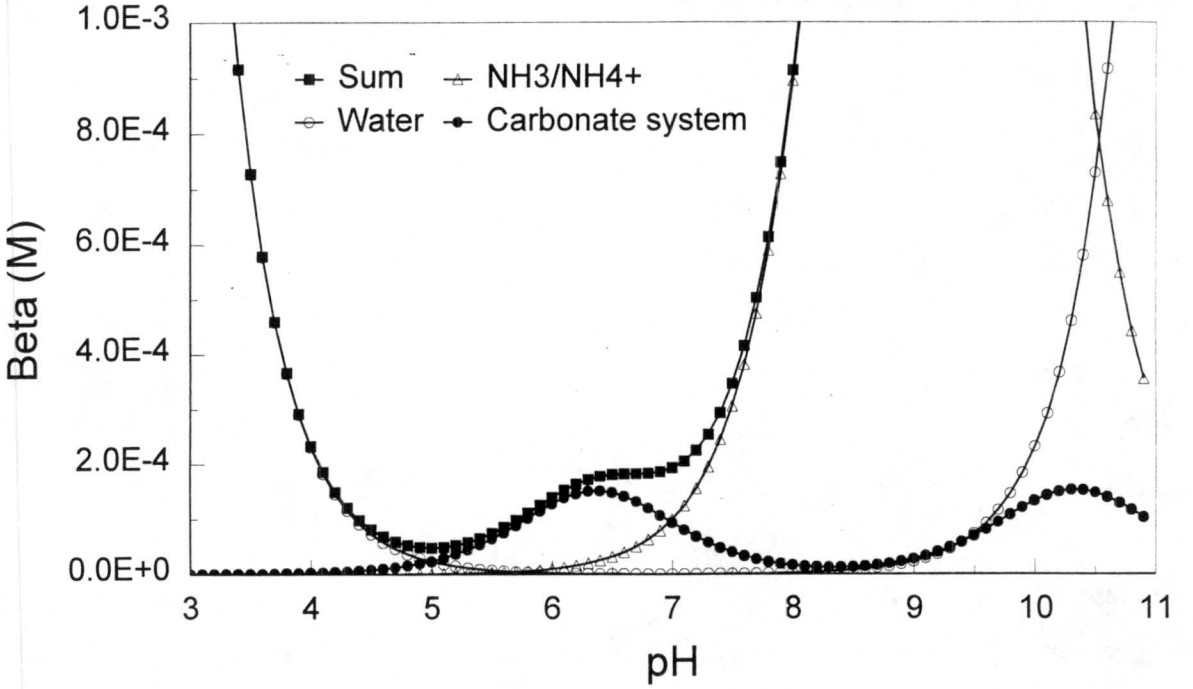

Figure 2.4. Theoretical buffering curves for four systems: pure water; dissolved ammonia and ammonium totaling 7.45 x 10^{-3} M; dissolved carbon dioxide, bicarbonate and carbonate totaling 2.64 x 10^{-4} M; and water containing the stated amounts of all species (sum).

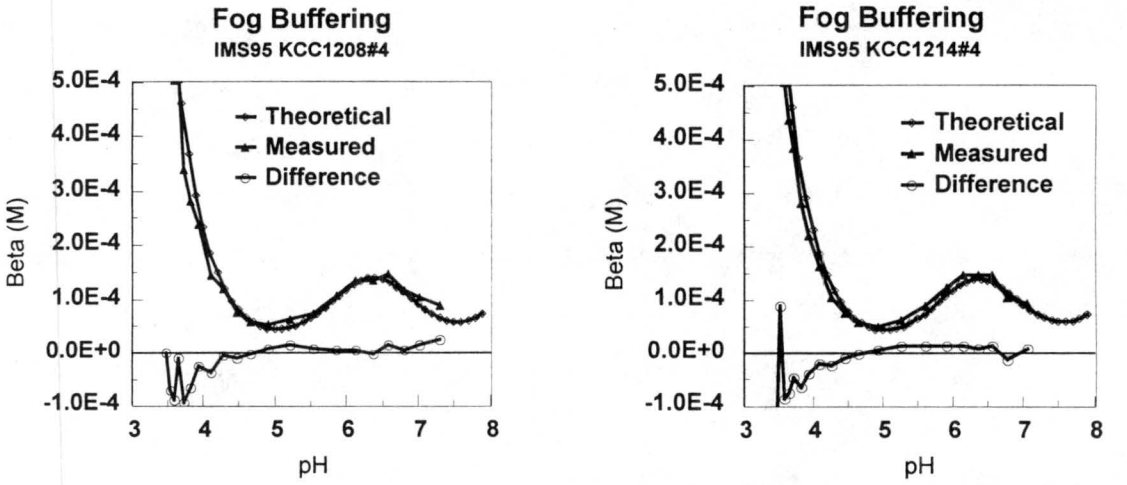

Figure 2.5. Buffering curves for two fog samples collected at the Kern Wildlife Refuge site during IMS95. Each plot shows a theoretical curve (based on measured bicarbonate and ammonium concentrations), a measured curve (from the acid titration of the sample) and a curve representing the difference between the measured and theoretical curves.

A strikingly different picture is observed in samples from Bakersfield and Fresno. At these locations, measured buffering curves frequently exhibit much more buffering than is predicted theoretically from the bicarbonate and ammonia concentrations. Figure 2.6 illustrates buffering curves for several Bakersfield fog samples from the 1994 study and from IMS95. The difference between the observed and theoretical curves is large and occurs over a broad pH range from approximately pH 4 to 7. This suggests that additional species are present in solution and acting as buffers. Three other Bakersfield samples (not shown) were analyzed in the same way, yielding similar patterns of unexplained buffering. Because the difference curves do not exhibit a single peak, it appears that either more than one additional, unknown buffering species is present or that one species is present which contains multiple chemical functionalities with pKa values in the range of 4-7. The control titrations made with water reveal that the unexplained buffering is already present in the fog samples and is not due to anything absorbed from the room air during titration.

Figure 2.7 shows buffering curves for fog samples collected during IMS95 at Fresno. Like the Bakersfield samples shown above, two of these three samples exhibit considerable unexplained buffering in the pH range from 4-7, while the third sample shows a smaller amount of unexplained buffering. Although the number of fog samples for which we have both the bicarbonate and ammonium analysis and a titration is small, the findings suggest that unexplained buffering may be more prevalent in urban locations (Bakersfield and Fresno) than at a rural location (KWR). This is a hypothesis that warrants further testing in future SJV fog sampling campaigns. While secondary inorganic aerosol species were observed to occur at similar levels in urban and rural fogs during IMS95, we did observe that several low molecular weight organic compounds were generally more concentrated in urban fogs. Together these patterns suggest that the unexplained buffering may be associated with an organic species of urban origin.

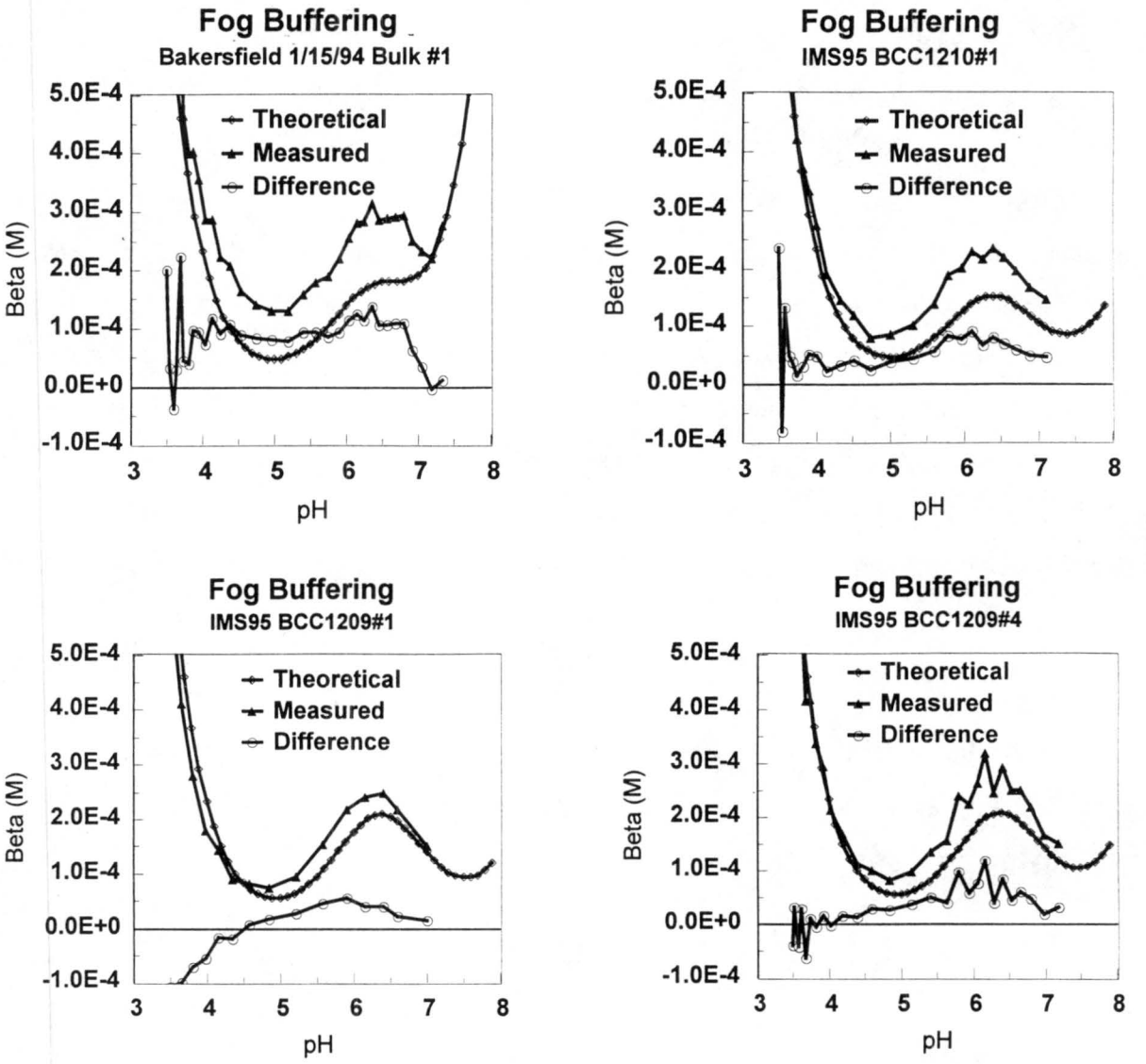

Figure 2.6. Buffering curves for four fog samples collected at Bakersfield, California. One sample was collected in 1994. The others were collected in 1995 during IMS95.

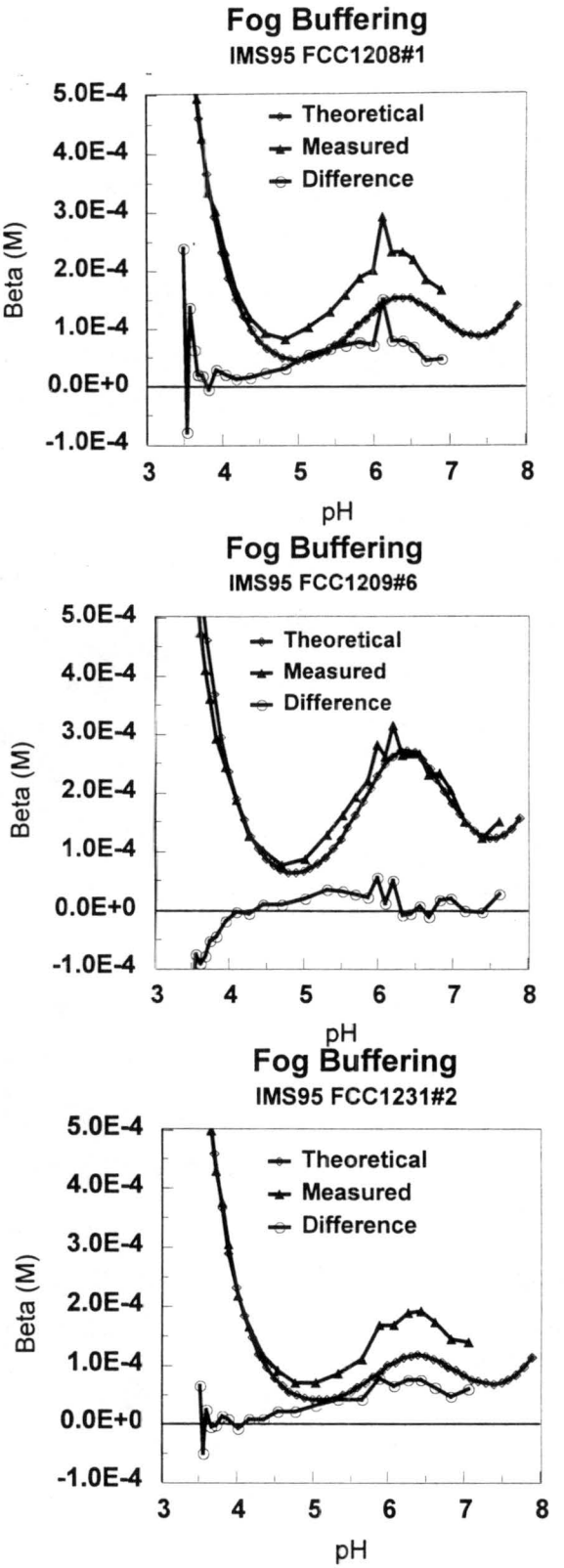

Figure 2.7. Buffering curves for fog samples collected at Fresno during IMS95.

Unexplained buffering quantification and correlation with measured species' concentrations

In order to quantify the amount of buffering present in the eleven special study fog samples, we integrated the area under each sample's unexplained buffering curve from the start of the titration down to pH 5. A lower limit of pH 5 was chosen to capture much of the unexplained buffering yet focus on the pH range typically found in SJV fog samples (pH > 5). The integrated area is a measure of the extra H^+ concentration which must be added to the sample to protonate the unknown buffering agents while lowering the fog sample pH to 5. This extra H^+ is in addition to that required to lower the sample pH to 5 in the presence of known buffering agents. The integrated area is presented for the eleven special study samples in Table 2.2 under the column entitled "unexplained buffering." The amount of unexplained buffering ranges from a high of 246 μM in one 1994 Bakersfield fog sample to a low of 27 μM in an IMS95 fog sample from the Kern Wildlife Refuge. The average amount of unexplained buffering in the fog samples was 153 μM at Bakersfield, 111 μM at Fresno, and only 29 μM at Kern Wildlife Refuge.

The amount of unexplained buffering in the fog samples was compared with concentrations of various measured species to see if any strong relationships were apparent. Correlation coefficients for these comparisons are presented in Table 2.3. Correlations between the amount of unexplained buffering and major ion (ammonium, nitrate, and sulfate) concentrations range from r^2=0.63 to r^2=0.65. Correlation vs. the sum of these three species (representative of the total major ion concentration) is no higher at r^2 = 0.65. Correlations of unexplained buffering vs. individual organic species' concentrations (measured in preserved fog sample aliquots analyzed a few weeks after collection) are higher, with correlation coefficients of 0.88, 0.66, and 0.75 for acetate, formate, and formaldehyde, respectively. Even higher correlations are found when some of these organic species' concentrations are summed (see Table 2.3). The best correlation (r^2 = 0.96) is found when correlating unexplained buffering vs. the sum of formate and acetate. Correlations vs. the sum of acetate and formaldehyde (r^2=0.91) and the sum of formate and formaldehyde (r^2=0.90) are nearly as strong. Although acetate and formate are buffering agents in the ambient fogwater, they were not present in the stored samples used for the August 1997 special sample titration study. Consequently, the strong correlations do not indicate that acetate and formate are themselves responsible for the unexplained buffering. Rather, the correlation

suggests that the species responsible for the unexplained buffering have concentrations that are strongly correlated with concentrations of measured low molecular weight organic species, particularly formaldehyde and acetate which were found to be strongly enriched in urban fogs. It seems likely, therefore, that the unknown buffering agents are also organic species produced primarily in the urban areas.

Table 2.3. Correlations of the amount of unexplained buffering vs. individual species' concentrations

Species	**Correlation Coefficient (r^2)**
Nitrate	0.63
Sulfate	0.65
Ammonium	0.65
Nitrate + Sulfate + Ammonium	0.65
Acetate	0.88
Formate	0.66
Formaldehyde	0.75
Acetate + Formate	0.96
Acetate + Formaldehyde	0.91
Formate + Formaldehyde	0.90
Acetate + Formate + Formaldehyde	0.94

Possible effects of sample storage on unexplained buffering

The determination that unexplained buffering exists in SJV urban fog samples is made from buffering and ion concentration measurements in stored fog samples. It is possible that some portion of the unexplained buffering present in the stored samples was added during storage. For example, one cannot absolutely rule out the possibility that microbial degradation of organic material in the fogwater produces new compounds that buffer against acidification in the region from pH 4 to 7. Unfortunately, it is difficult in a field setting to obtain all the information necessary to quantify the amount of unexplained buffering present in a sample. As pointed out above, the inorganic carbon concentration present in fog samples can change readily with

changes in sample temperature or storage conditions, and no on-site measurements of fogwater bicarbonate concentrations are available from these studies. Estimates of the buffering contribution from bicarbonate (made from equilibrium calculations using typical atmospheric carbon dioxide concentrations), however, reveal the presence of buffering above pH 4 that is not explained by the presence of calculated inorganic carbon concentrations or measured concentrations of formate, acetate, and ammonia/ammonium. Further, storage procedures for the rural (KWR) samples were the same as those for fog samples from the urban sites. Likewise, microbial degradation of low molecular weight organic carboxylic acids occurred in both the rural (KWR) and urban (Bakersfield and Fresno) fog samples. However, significant unexplained buffering was found only in the urban fog samples. These observations suggest that agents responsible for the unexplained buffering were present at the time of sample collection rather than being added as a result of sample transformation during storage. Future studies in the region should attempt to verify this conclusion by quantifying contributions of known buffering agents as accurately as possible immediately after sample collection.

Further buffering agent characterization

We have conducted a number of investigations to gather information about the nature of the compounds responsible for the unexplained buffering. In titration tests involving filtered and unfiltered fogwater, no significant difference was observed between acid buffering present in filtered and unfiltered fog sample aliquots, indicating that the unknown buffering agent(s) is present in dissolved form. Figure 2.8 illustrates this result for several samples.

Analysis of several 1994 Bakersfield samples revealed no significant amounts of phosphate (pK_{a_2} for phosphoric acid is approximately 7.2) in the fogwater. Measurements of aqueous S(IV) also reveal that free S(IV) is not present at high enough concentrations for protonation of sulfite or bisulfite to contribute significant acid buffering.

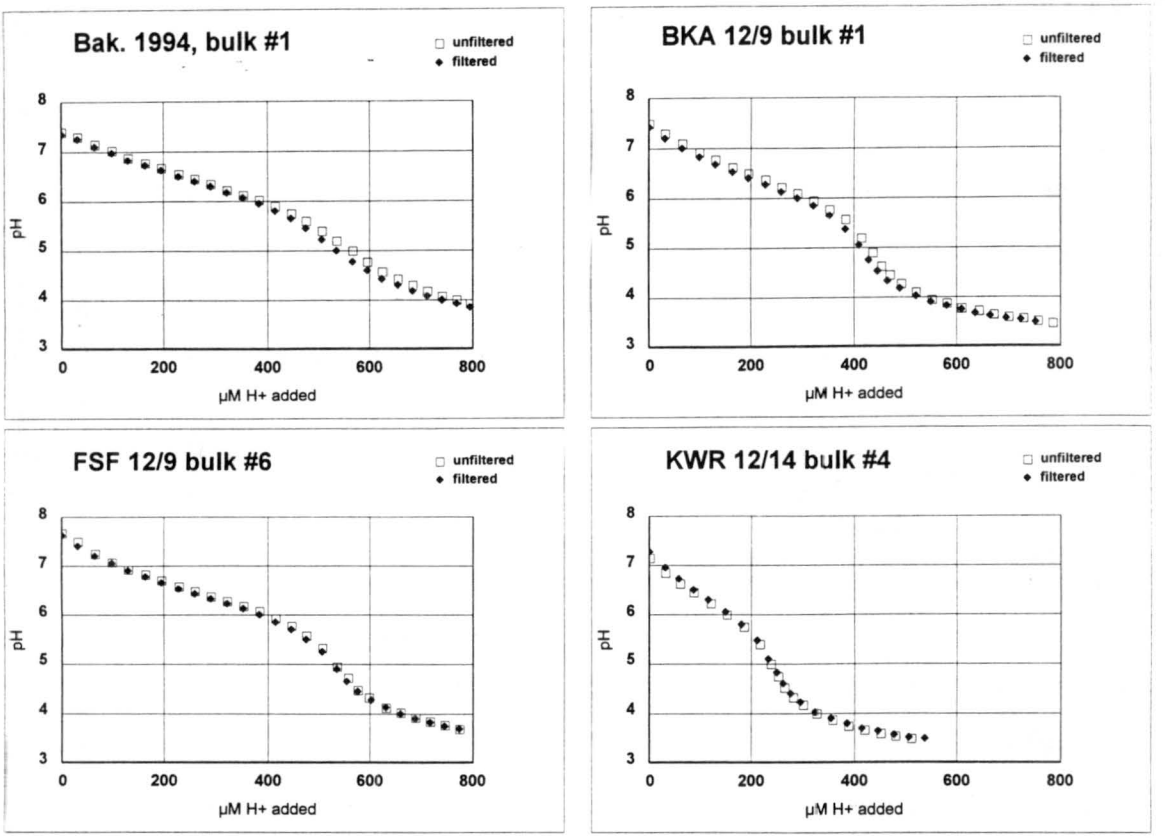

Figure 2.8. Titrations of filtered and unfiltered aliquots of fog samples characteristic of each site.

A number of investigators (Tremp, 1992; Levsen et al., 1993; Luettke et al., 1997) have reported finding significant concentrations of substituted phenols, especially nitrated phenols, in polluted fogs and clouds sampled in Europe. Several of these compounds have pKa's in the range where the unexplained buffering occurs in SJV fog samples, so we prepared a fog sample for phenols analysis. Analytes of particular interest in the EPA method 604 phenols analysis are phenol, 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol, which have been reported at substantial concentrations in polluted fog elsewhere. These compounds were found to exist in the composite SJV fog sample only at trace levels (4-nitrophenol and 2,4-dinitrophenol were present at 4.1 and 16.4 µg/l, respectively) or were not present at levels above the method detection limit (phenol and 2-nitrophenol were not detected; MDL = 1.0 µg/l for both compounds). Complete results are presented in Table 2.4. The observed concentrations are not high enough to provide any significant acid buffering. This does not rule out possible buffering contributions from large methoxyphenols produced as a result of wood combustion. Schauer (1998) found that wood

burning was an important source of primary organic carbon particulate matter in the SJV during IMS95.

Other compounds that could contribute to the unexplained buffering include humic material and dicarboxylic acids. Havers et al. (1998) have shown that humic-like substances are important constituents of the organic carbon present in aerosol particles. Titrations of humic acids reveal a variety of pKa's present in the range pK 4-8 (Jin-Zhou et al., 1994). The pKa's, corresponding to different functional groups on the humic acid, roughly span the range of unexplained buffering observed in the SJV fog samples. UV/Visible absorption spectra of the fog samples showed no significant peaks except a gradual increase in absorption at wavelengths below 400 nm, similar to absorption spectra reported by Havers et al. (1998) for several humic-like substances. More definitive tests of the presence and characteristics of humic substances in San Joaquin Valley fogs will require much greater volumes of fogwater than are currently available.

Ludwig and Klemm (1988) investigated the contributions of several organic acids found in atmospheric aerosol particles in northern Bavaria, Germany, to buffering of aqueous aerosol extracts. Weak organic acids were not found in rural aerosol samples. Several dicarboxylic acids, including succinic acid, glutaric acid, 2-oxoglutaric acid and adipic acid, were found in several urban and some suburban aerosol samples. Ludwig and Klemm's HPLC analysis also revealed the presence of three unidentified organic acids in many of these samples. pKa's for several of the identified acids fall in the range from 4.3 to 5.6, suggesting they could play an important role in buffering against acidification of fog drops over a pH range from below 4 to above 6. This overlaps closely with the lower and mid-pH range of the unexplained buffering we observed in the urban SJV fog samples. The presence of these weak organic acids only in urban and suburban samples in Ludwig and Klemm's (1988) study is also consistent with our observation that little unexplained acid buffering was present in fog samples from the rural KWR site.

Table 2.4 Measured phenols concentrations in composite SJV fog sample

Parameter	Concentration (µg/l)	Method Detection Limit (µg/l)
4-chloro-3-methylphenol	ND*	1.00
2-chlorophenol	ND	1.00
2,4-dichlorophenol	ND	1.00
2,4-dimethylphenol	0.76	1.00
2,4-dinitrophenol	16.4	5.00
4,6-dinitro2mephenol	10.1	5.00
2-nitrophenol	ND	1.00
4-nitrophenol	4.13	1.00
Pentachlorophenol	ND	1.00
Phenol	ND	1.00
2,4,6-trichlorophenol	ND	1.00

*not detected

3. Modeling of acid buffering and its effects

All atmospheric aqueous-phase chemistry models calculate the pH of the fog/cloud by solving the electroneutrality equation during each computational step. The equation can be written as

$$ANC + [H^+] + \sum_{k=1}^{p} [BH^+]_k - [OH^-] - \sum_{l=1}^{q+r} [HD^-]_l - 2\sum_{m=1}^{r} [D^{2-}]_m = 0 \qquad (4)$$

where ANC is the acid neutralizing capacity of the solution (difference between the concentrations of the strong base cations and the strong anions), $[BH^+]_k$ is the concentration of the k^{th} base, $[HD^-]_l$ is the concentration of the l^{th} acid that dissociated once, and $[D^{2-}]_m$ is the concentration of the m^{th} acid that dissociated twice. Here we assume that there are p weak bases, q weak acids that dissociate once, and r weak acids that dissociate twice. By using the dissociation equilibria relationships for the various acids and bases the above equation can be rewritten in the form

$$f([H^+])=0 \qquad (5)$$

namely one nonlinear algebraic equation with one unknown, the concentration of H^+. For example, for the dissolved SO_2 ionic species:

$$[HSO_3^-] = \frac{1}{1 + \frac{[H^+]}{K_{s1}} + \frac{K_{s2}}{[H^+]}} [S(IV)] \qquad (6)$$

$$[SO_3^{2-}] = \frac{1}{1 + \frac{[H^+]}{K_{s2}} + \frac{[H^+]^2}{K_{s2}K_{s1}}} [S(IV)] \qquad (7)$$

where K_{s1} and K_{s2} are the first and second dissociation constants of $SO_2.H_2O$ and S(IV) is defined as

$$[S(IV)] = [SO_2.H_2O] + [HSO_3^-] + [SO_3^{2-}] \quad (8)$$

The above example indicates that including the buffering effect of an acid or a base in an atmospheric chemistry model requires in general knowledge of its total concentration and of its dissociation constant(s) or pK_a values. The preceding analysis indicated that the observed unexplained buffering intensity could not be explained by the hypothesis of a single unknown buffering agent. We attempted to reproduce the observed buffering intensity with up to four individual species but the results were unsatisfactory. We elected instead to use an empirical function $b(H^+)$ in the electroneutrality equation that would simulate the unexplained buffering intensity. After some experimentation we found that a logarithmic function of the form

$$b(H^+) = a \log_{10} [H^+] \quad (9)$$

where a is a constant, could reproduce the observed buffering behavior of the SJV fog samples.

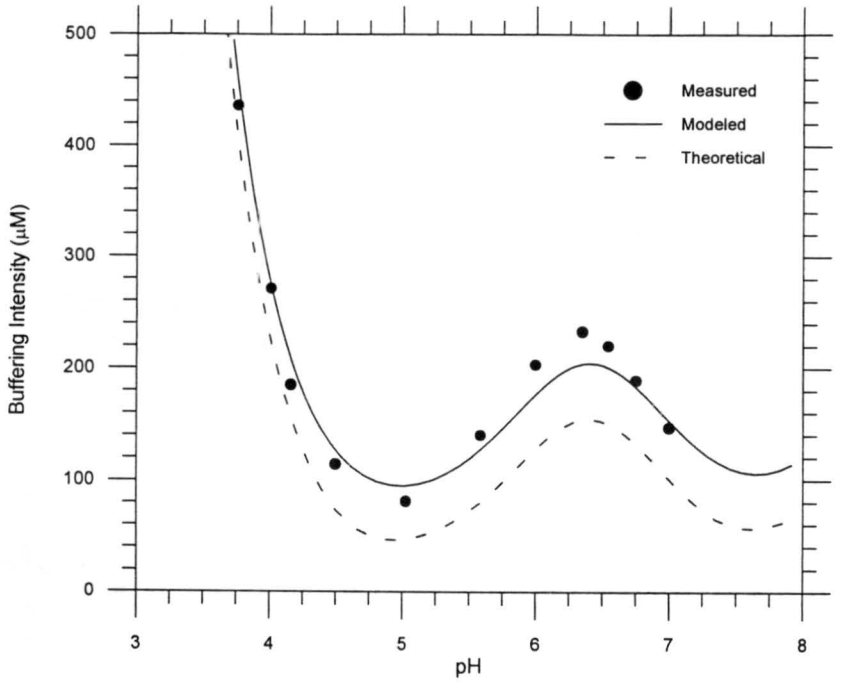

Figure 3.1. Measured buffering intensity (solid symbols), theoretical buffering intensity accounting for ammonia and carbonates, and modeled intensity including ammonia, carbonates, and the unexplained buffering agent(s). The sample is from the fog episode of December 10, 1995 in Bakersfield.

This empirical expression was then added to the electroneutrality equation used in the fog model of Pandis and Seinfeld (1989). The model was then calibrated using the laboratory measurements of the CSU group. For example, for a sample collected during the December 10 fog episode in Bakersfield using the measured carbonate and ammonium concentrations and neglecting the additional buffering the model predicts the buffering intensity shown in Figure 3.1. After adding the unexplained buffering intensity using the above empirical expression (using a = 50 μM) the predictions of the model agree well with the CSU laboratory measurements (Figure 3.1). The aqueous-phase module with the adjusted buffering capacity was then used to simulate the fog episode of that night in Bakersfield. The radiation fog model and the simulation results neglecting this additional buffering capacity have been discussed by Pandis and Cruz (1997) and will only be summarized in this study.

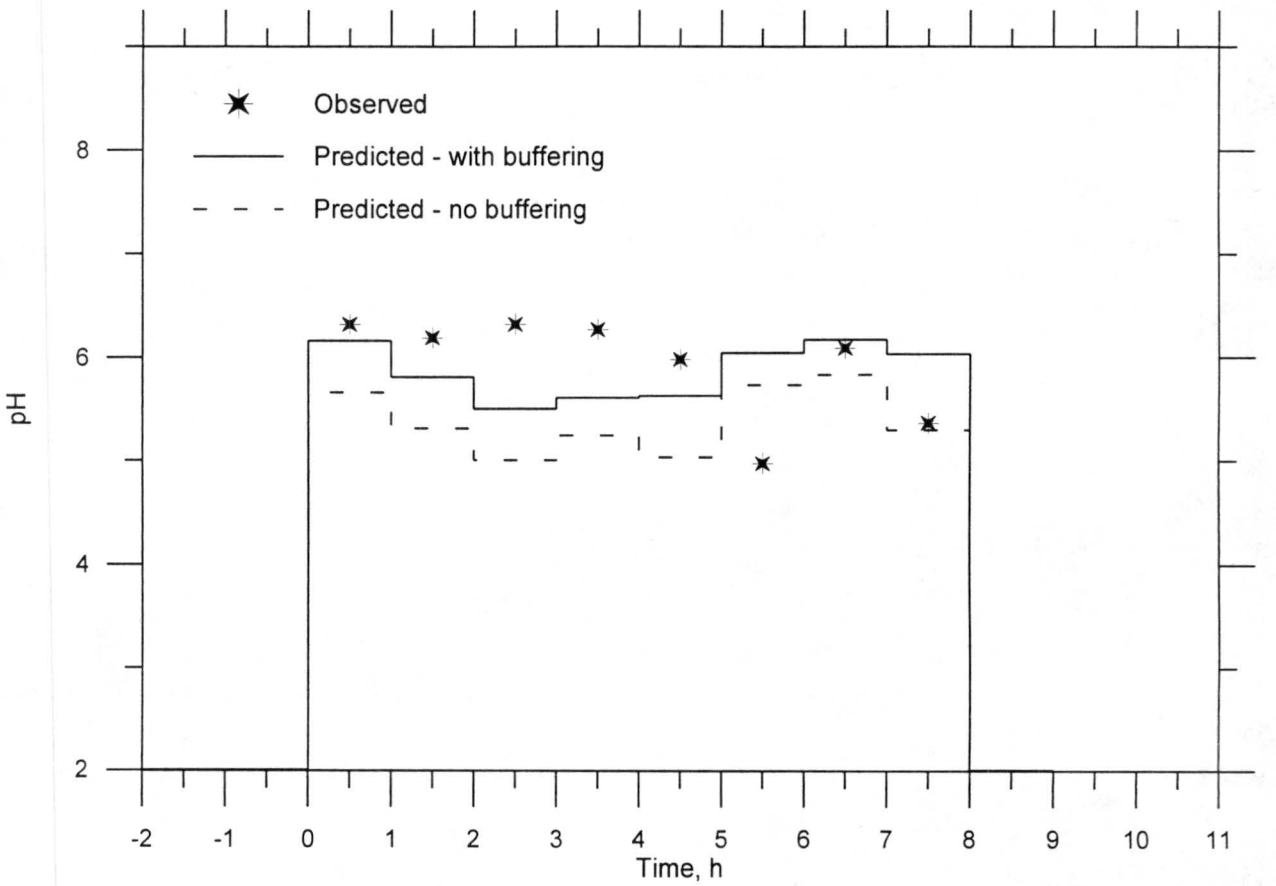

Figure 3.2. Predicted pH for the fog episode of December 10, 1995 in Bakersfield (a) neglecting the additional (unexplained) buffering intensity, (b) including this additional buffering effect. Also shown are the measurements during the fog episode.

Effect on Aqueous-Phase Chemistry

The radiation fog chemistry model predictions for the fog episode during the morning of December 10 are depicted in Figure 3.2. Including the additional buffering effect results in an increase of the predicted fog pH by 0.3-0.7 pH units. In general this change improves the agreement of the model with observations for most of the fog episode. Exceptions to this trend are the periods from 5 to 6 am when the site was influenced by a local plume (there was a sudden change in wind direction) (Pandis and Cruz, 1997), and the last hour of the fog episode. The predicted pH effect is significant for the high pH fogs of the SJV.

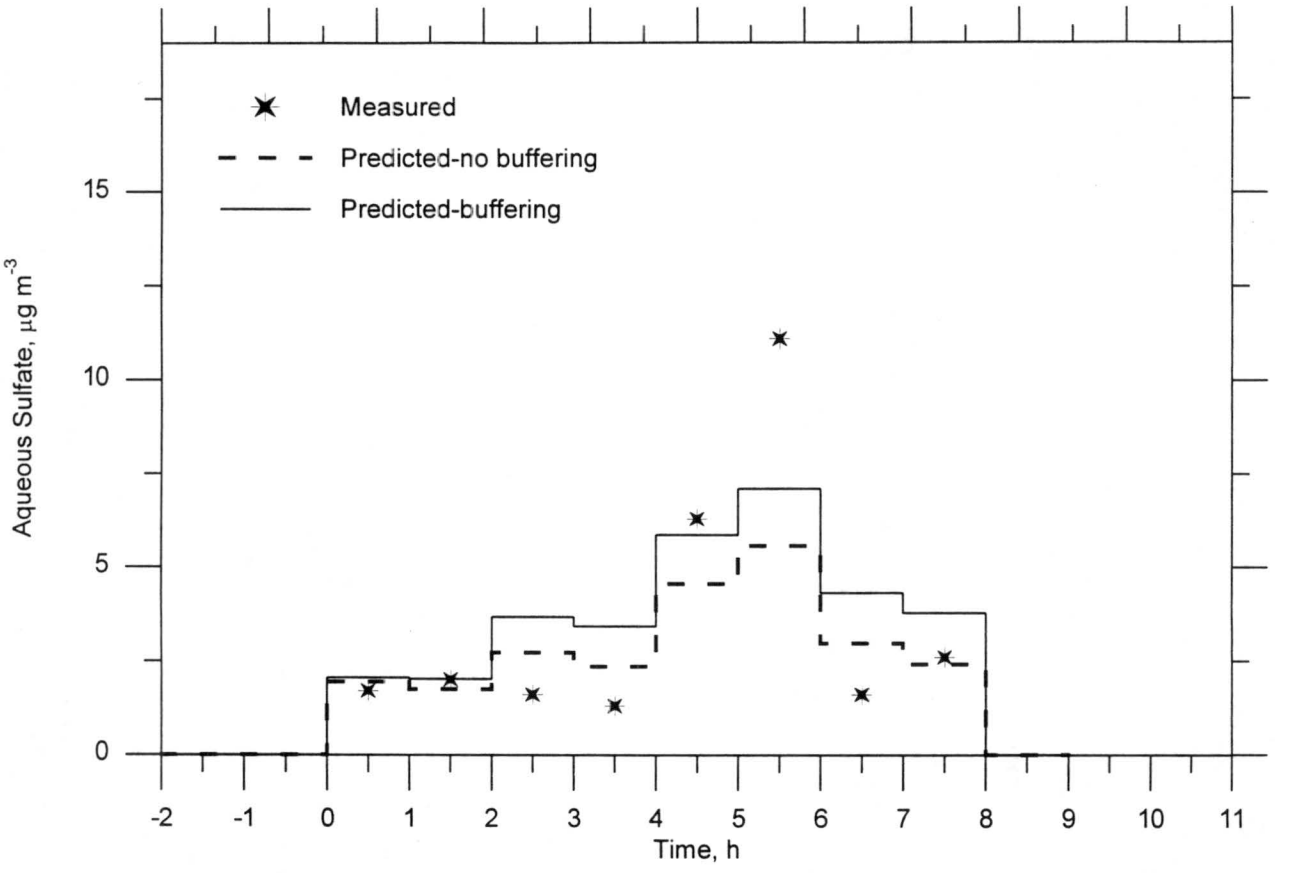

Figure 3.3. Predicted sulfate concentrations for the fog episode of December 10, 1995 in Bakersfield (a) neglecting the additional buffering intensity, (b) including this additional buffering effect. Also shown are the measurements during the fog episode.

The change in fog pH accelerates the formation of sulfate in the fog layer. The model predictions are compared to the predictions without the additional buffering and the measurements in Figure 3.3. An increase of the predicted sulfate concentration by 10-60% is indicated by the comparison of these simulations. The effect of the additional buffering is an increase of the ambient sulfate concentration after the fog episode by approximately 50%. These results indicate that the additional buffering can have a significant impact on the sulfate production during these fog episodes. Finally adding the extra buffering does not change significantly the net agreement (or lack thereof) of the model predictions with observations. For some periods (12-2, 4-6 a.m.) the agreement improves while for the rest it deteriorates.

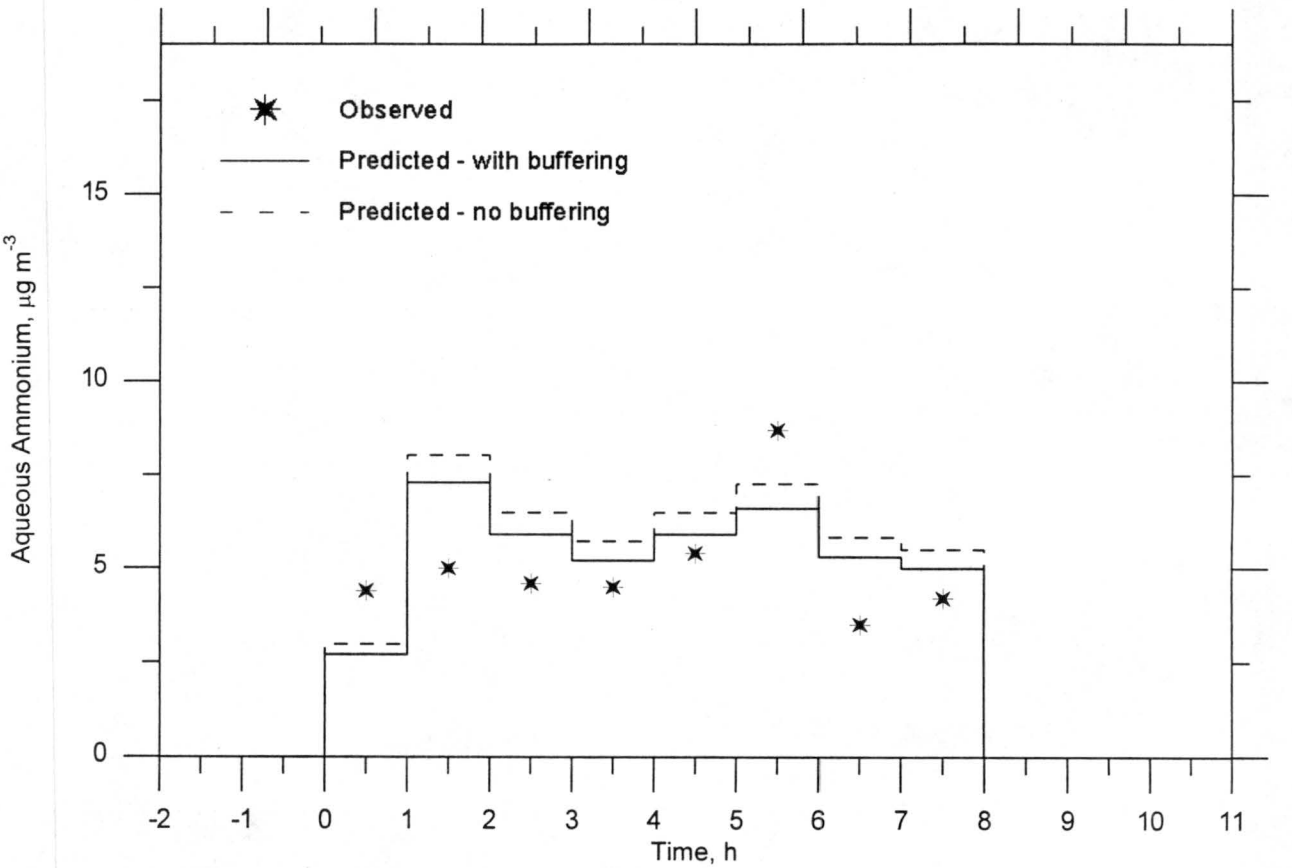

Figure 3.4. Predicted ammonium concentrations for the fog episode of December 10, 1995 in Bakersfield (a) neglecting the additional buffering intensity, (b) including this additional buffering effect. Also shown are the measurements during the fog episode.

Including the additional buffering capacity in the model did not affect the predicted nitrate concentrations. For the pH range of these fog episodes practically all the nitric acid inside the fog

layer is dissolved in the aqueous-phase. The pH increase caused by the additional buffering does not therefore influence the partitioning of nitrate between the gas and aqueous phases. The only significant aqueous-phase reaction affecting the nitrate concentrations inside the fog layer is the NO_3/N_2O_5 heterogeneous reaction with liquid water. We have assumed that this reaction is rapid enough so that it is limited by the mass transfer rate of these species to the droplet surface, and therefore that its rate is not dependent upon the fog pH. As a result the production and removal rates of nitrate in the fog layer, according to our current understanding, are not sensitive to the buffering capacity of the fog water.

The effect of the additional buffering on the predicted ammonium concentrations in fog water is illustrated in Figure 3.4. Including the buffering effect in the calculations increases the predicted pH resulting in a shift of the ammonia partitioning towards the gas-phase and reducing the fog water ammonium concentrations. However this change is partially balanced by the slower removal of ammonium by wet deposition. The net effect is a small decrease of the predicted ammonium concentrations of the order of 10% or less. This change improves slightly the agreement of the model with observations (Figure 3.4).

The predicted effect of the additional buffering capacity is a sensitive function of the ozone concentration inside the fog layer. For the previous simulations we assumed that the ozone concentration inside the fog layer is the measured value of 5 ppb. If the concentration is zero (as predicted by the gas-phase chemistry module) then the most important sulfate reaction pathway is the pH-independent reaction with hydrogen peroxide, and the unknown buffering has a minor effect on the sulfate production. The sensitivity of the predicted fog water sulfate to the assumed (small) ozone concentration including the buffering effect is shown in Figure 3.5. Note that at the peak sulfate concentration even a small change in ozone (as small as 0.5 ppb) has a significant effect. The buffering effect becomes more significant for lower hydrogen peroxide concentrations (a 0.8 ppb concentration, on the upper end of typical values observed during IMS95, has been assumed for these simulations).

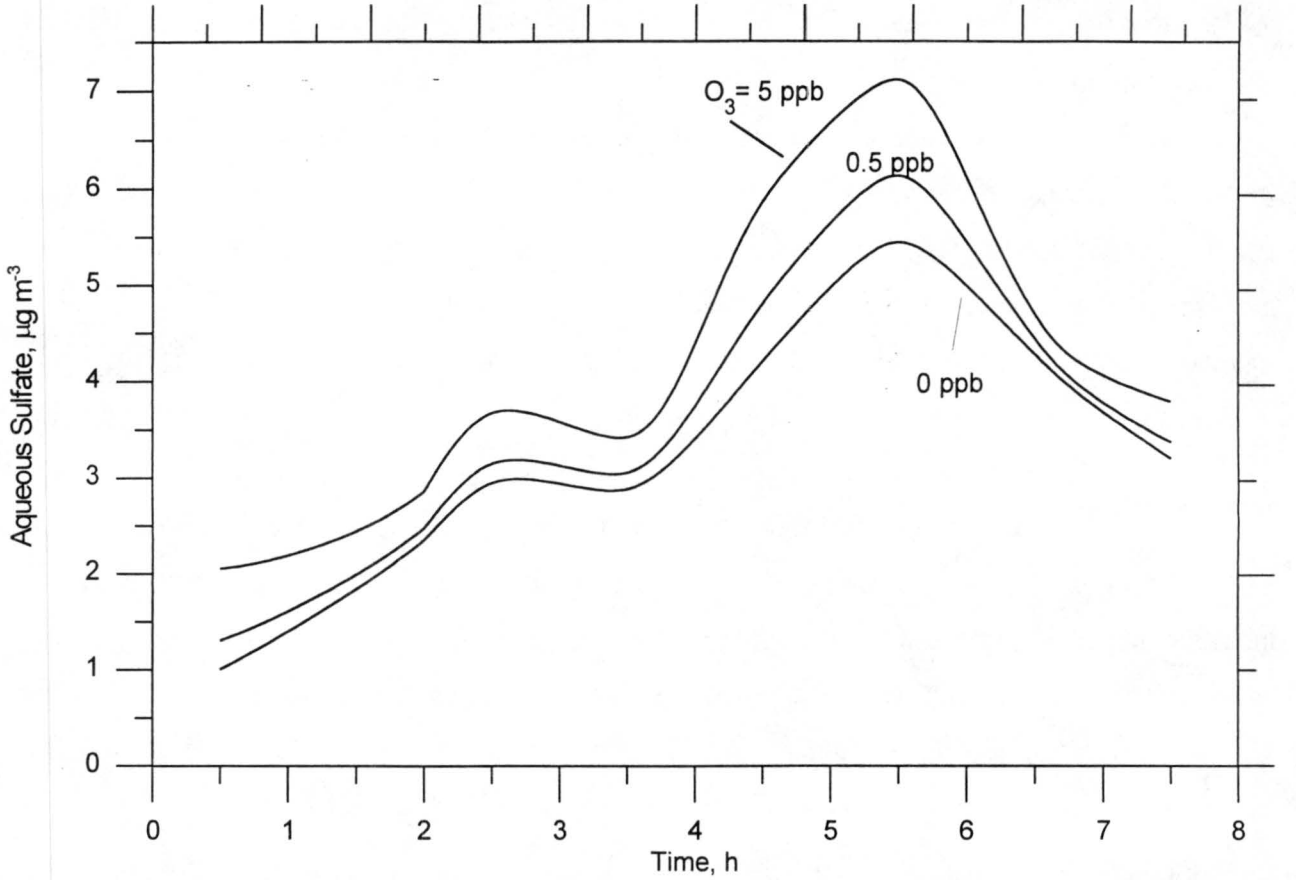

Figure 3.5. Effect of the ozone concentration inside the fog layer on the predicted sulfate concentration for the fog episode of December 10, 1995 in Bakersfield.

4. Summary and conclusions

Sulfate production in San Joaquin Valley (SJV) fogs occurs largely through oxidation of S(IV) by ozone. This pathway is very pH dependent. At higher pH, more sulfur dioxide is present in the liquid phase at equilibrium and it is partitioned into forms that react more rapidly with ozone. As S(IV) is oxidized to sulfuric acid, protons are released into solution causing the droplet pH to decline. For a pure water drop initially at pH 7, very little acid production is required to quickly acidify the drop to pH 5 (requires only 10 μM acid) or below. There are known to be several weak acids and bases present in solution, however, which can buffer against pH decreases. For example, dissolved carbon dioxide exists in fog drops. At pH 7 it is present mainly as bicarbonate. As protons are introduced to the solution, the bicarbonate can be protonated to carbonic acid, thereby removing free protons from solution and buffering against a rapid drop in pH. This buffering will be strongest at the point where there are equal amounts of bicarbonate and carbonic acid. This corresponds to the point where the droplet pH is equal to the pKa of carbonic acid. Other species in solution that can accept protons and buffer against pH declines include ammonia, acetate, and formate. These buffering agents provide what might be called internal buffering. External buffering, provided by species which partition from the gas phase into the drops in response to declining pH, is also possible. A classic example of external buffering is absorption of ammonia, which is protonated to ammonium upon entering neutral or acidic drops.

Acid titrations of numerous San Joaquin Valley fog samples, collected during IMS95 and in previous investigations, reveals that considerable internal acid buffering capacity is present in SJV fogs. Tests reveal that in the rural Kern Wildlife Refuge fogs the internal buffering can be nearly accounted for by measured concentrations of bicarbonate and ammonia/ammonium. In urban fog samples from Bakersfield and Fresno, however, insufficient concentrations of bicarbonate, ammonia, acetate, and formate were present to account for the observed buffering in most cases examined. A comparison of measured and theoretical buffering curves suggest that one or more unknown buffering agents are present in solution and provide significant buffering across a broad pH range from approximately 4-7. The fact that we don't observe one, or even a few, defined peaks in this additional buffering, suggests that several compounds with a variety of

pKa's or one compound containing a variety of functional groups possessing a variety of pKa's are likely responsible.

A number of investigations have been conducted to attempt to characterize the unknown buffering agent(s). Comparisons of buffering in filtered vs. unfiltered fog sample aliquots reveal that the buffering agents are dissolved in solution. Analyses reveal that phosphate is not present at a sufficient level to explain any significant portion of the observed, unexplained buffering. The fact that the buffering is greater in urban fogs, which also were observed to be enriched in organic material, suggests that the unknown buffering agents might be organic in nature. This hypothesis is supported by observations that the amount of unexplained buffering is strongly correlated with the sum of concentrations of low molecular weight organic compounds (formate, acetate, and formaldehyde) measured in the fogwater. Several substituted phenols, which have pKa's in the range of 4-7 have been observed at significant concentrations in polluted European fogs and clouds. Analyses of phenols in a composite SJV fog sample, however, revealed that they were only present at trace concentration levels, insufficient to provide significant buffering. Humic acids are known to buffer across a wide pH range, including the pH range observed here. They remain candidates for the unknown buffering agents. Characterization of the structure of humic material in fogwater is possible, but would require many liters of fogwater, which is not presently available. Dicarboxylic acids may also contribute a portion of the unexplained buffering, especially in the pH range from 4 to 6.

A method was found to include the additional, unexplained fog sample buffering in the Carnegie Mellon University fog model used to simulate IMS95 fog episodes. Because the buffering occurred over a broad pH range, it was not possible to satisfactorily simulate it in the model by adding a few, hypothetical buffering agents. Instead, an empirical buffering function was formulated and included in the electroneutrality equation solved by the model. This method yielded good agreement between the observed and model-simulated buffering. Simulations of the effect of the additional buffering in the December 10, 1995 fog episode at Bakersfield revealed a significant impact on the fog chemistry. The additional buffering permitted the fog pH to remain 0.3-0.7 pH units higher than predicted in a simulation without the additional buffering. As a result, the rate of S(IV) oxidation by ozone was significantly enhanced, leading

to an increase in sulfate aerosol present following the fog episode of approximately 50%. The buffering had no effect on nitrate concentrations and only modest (~10%) effects on ammonium concentrations.

The apparent importance of the buffering to sulfate production suggests that it needs to continue to be investigated in future SJV fog campaigns. Several items are recommended which would improve our understanding of the buffering and its impacts on aerosol formation in SJV fogs.

It would be better to titrate at least some samples in the field immediately after collection. It is possible that reactions occur in fog samples during storage that may increase or decrease the buffering. Sample pH also commonly increases within a couple days after collection (due to microorganisms consuming organic acids in solution). This can lead to changes in partitioning of important gases (e.g., carbon dioxide and ammonia) between the fog sample and the air in the sample bottle and in the storage facility. Because indoor carbon dioxide concentrations typically greatly exceed outdoor concentrations, samples can absorb additional carbon dioxide after collection when handled or stored indoors. For this reason, it is recommended that field titrations be conducted outside, accompanied by simultaneous measurements of carbon dioxide and temperature. In general, we have found that measurements of acid buffering are of little value without knowing the amounts of bicarbonate, ammonia, and low molecular weight organic acids present in solution.

Further work is needed to examine whether the pattern observed here, where unexplained buffering was observed mainly in urban fogs, is general. Measurements of total organic carbon in all samples selected for buffering analysis would also permit the correlation between unexplained buffering amounts and the total organic content of the fogs.

Future efforts should include an attempt to collect large volumes of fogwater for analysis of organic solutes. Further phenols analysis is recommended along with analysis of humic acids and dicarboxylic acids in solution. Additional speciation of organic compounds present in solution via improving GC-MS and LC-MS approaches might also lead to identification of other candidate buffering agents.

Understanding the role of the additional buffering in future SJV fog studies would, of course, benefit by further model simulations of those episodes. While the model simulations predict that ozone will be removed from the system by reaction with NO and not regenerated at night, ozone monitors revealed small, but non-zero amounts of ozone in the IMS95 fog episodes. Further work is recommended to verify the accuracy of ozone gas measurements at levels below 5 ppb. This issue is critical because the rate of sulfate production and the role of buffers in enhancing that production is extremely sensitive to the amount of ozone available, the droplet pH, and the hydrogen peroxide concentration. If ozone concentrations are actually lower than the reported values, sulfate production will slow and hydrogen peroxide will be the dominant oxidant. In this case the buffering is of little consequence since S(IV) oxidation by hydrogen peroxide is pH independent in the pH range found in SJV fogs.

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