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THE GEOCHEMICAL CYCLING OF REACTIVE CHLORINE THROUGH THE MARINE TROPOSPHERE

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Abstract. Heterogeneous reactions involving sea-salt aerosol in the marine troposphere are the major global source for volatile inorganic chlorine. We measured reactant and product species hypothesized to be associated with these chemical transformations as a function of phase, particle size, and altitude over the North Atlantic Ocean during the summer of 1988. Concentrations of HCl were typically less than 1.0 ppbv near the sea surface and decreased with altitude and with distance from the U.S. east coast. Concentrations of Cl volatilized from aerosols were generally equivalent to the corresponding concentrations of HCl and ranged from less than detection limits to 125 nmol m^{-3} STP. Highest absolute and percentage losses of particulate Cl were typically associated with elevated concentrations of anthropogenic combustion products. Concentrations of product nss SO_4^{2-} and NO_3^- in coarse aerosol fractions indicate that on average only 38% of measured Cl^- deficits could be accounted for by the combined effects of acid-base desorption and reactions involving nonacidic N gases. We hypothesize a mechanism for the Cl loss initiated by reaction of O_3 at sea-salt aerosol surfaces, generating Cl_2, followed by rapid photochemical conversion of Cl_2 to HCl via Cl atoms (Cl·) and eventual recapture of HCl by the aerosol. Simulations with a zero-dimension (0-D) photochemical model suggest that oxidation by Cl· may be an important tropospheric sink for dimethyl sulfide and hydrocarbons. Under low-NO_x conditions, the rapid cycling of reactive Cl would provide a catalytic loss mechanism for O_3, which would possibly explain the low O_3 concentrations often observed above the world's oceans.

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1. INTRODUCTION

The injection of sea-salt aerosol generated by breaking waves on the ocean's

surface is the major global source for atmospheric Cl [Erickson and Duce, 1988]. Most of this Cl remains in the aerosol and is returned to the ocean surface via dry and wet deposition, but important fractions, ranging from 3 to 20% on average, are released from the aerosol as inorganic Cl vapor (Cl^i_g) [e.g., Cicerone, 1981]. Although this particle-to-gas conversion is by far the major source for gaseous Cl in the global troposphere [e.g., Friend, 1989], decades of research have failed to demonstrate conclusively the primary mechanism(s) involved. This is due in part to the fact that few studies have measured principal reactant and product species simultaneously as a function of phase and particle size in marine regions remote from continental influences.

HCl is generally recognized as the major fraction of Cl^i_g in the marine troposphere [Ryan and Mukherjee, 1974; Wofsy and McElroy, 1974]. Thermodynamic considerations coupled with field measurements of aerosol chemistry and Cl^i_g suggest that most of the HCl may originate with direct volatilization from sea-salt aerosol which is acidified to low pH (<3) by the incorporation of HNO_3 and H_2SO_4 (Eriksson, [1959], Duce, [1969], Martens et al. [1973], Berg and Winchester [1977], Kritz and Rancher [1980], Brimblecombe and Clegg [1988], Legrand and Delmas [1988], Wall et al. [1988], among many others) as follows:

$$HNO_{3(g)} + NaCl_{(p)} \rightarrow HCl_{(g)} + NaNO_{3(p)} \quad (1)$$

$$H_2SO_{4(p)} + 2\ NaCl_{(p)} \rightarrow 2\ HCl_{(g)} + Na_2SO_{4(p)} \quad (2)$$

Although exchange between particulate-phase Cl^- and Cl^i_g has been demonstrated clearly by extensive field measurements, the importance of the acid-base desorption mechanism as the principal driver for Cl phase change in the marine troposphere remains open to question [e.g., Cicerone, 1981; Friend, 1989].

Alternative mechanisms involving reactions of various N gases with sea-salt aerosol have also been suggested as sources for chemically active halogen gases in the marine troposphere. Reaction of NO_2 with sea-salt aerosol has been hypothesized [Altshuller, 1958] and demonstrated to be a source for Cl^i_g [Schroeder and Urone, 1974; Finlayson-Pitts, 1983] as follows:

$$2\ NO_{2(g)} + NaCl_{(p)} \rightarrow NOCl_{(g)} + NaNO_{3(p)} \quad (3)$$

NOCl has short lifetimes against photolysis (5-30 min) and hydrolysis (0.03 s to 45 min). Photolysis of NOCl generates Cl atoms (Cl·) which may then initiate oxidation of hydrocarbons to produce HCl. Hydrolysis of NOCl generates $HONO_{(g)}$, a source of OH radical (OH·), and HCl. In both cases, the final products of these rapid reaction sequences are HCl and $NaNO_3$, the same products expected from an acid-base desorption involving HNO_3 (reaction (1)). Finlayson-Pitts et al. [1989] recently reported that $ClNO_3$ and N_2O_5 react with NaCl aerosol to generate reactive Cl^i_g as follows:

$$ClNO_{3(g)} + NaCl_{(p)} \rightarrow Cl_{2(g)} + NaNO_{3(p)} \quad (4)$$

$$N_2O_{5(g)} + NaCl_{(p)} \rightarrow ClNO_{2(g)} + NaNO_{3(p)} \quad (5)$$

Rapid photolysis of product Cl_2 and $ClNO_2$ generates Cl· and ultimately HCl through subsequent reactions. Again, the final products are HCl and $NaNO_3$. Considerable uncertainties exist in assessing the potential for a significant influence of reactions (3), (4), and (5) in the remote marine troposphere, but given the expected and observed concentrations of reactant N gases [e.g., Levy and Moxim, 1989], it has been suggested that such transformations will be an important source for Cl^i_g only in more polluted regions [e.g., Singh and Kasting, 1988].

The nature of heterogeneous reactions which generate Cl^i_g have important implications for marine tropospheric chemistry. For instance, transformations involving NO_2, $ClNO_3$, and N_2O_5 generate highly reactive Cl compounds which can initiate photochemical reactions in an analogous manner to ·OH, whereas acid-base desorption generates relatively unreactive HCl. The modeling investigation of Singh and Kasting [1988] suggests, however, that if ppbv concentrations of HCl are generated by any mechanisms, reaction with ·OH can produce sufficient Cl· to photooxidize a significant fraction (20 to 40%) of nonmethane alkanes in the marine troposphere. It is clearly essential that the compounds involved, mechanisms of emission, and rates of reaction be identified unequivocally if we are to understand major processes in the chemical cycling of S, N, C, odd O, odd H, and Cl through this dynamic system.

The present study was designed to measure major reactant and product species

which are thought to be involved in the heterogeneous generation of Cl_g^i from reactions involving sea-salt aerosol in the marine troposphere. Hypothesized sources are assessed in light of these data.

2. METHODS

Bulk- and size-segregated samples of atmospheric aerosol, some with simultaneous samples of alkaline reactive Cl, N, and S gases (hereinafter referred to as HCl, HNO_3, and SO_2, respectively), were collected from an aircraft and a ship over the North Atlantic Ocean (NAO) during the summer of 1988 as part of the Global Change Expedition, Coordinated Air-Sea Experiment, and Western Atlantic Ocean Experiment (GCE/CASE/WATOX) [Pszenny et al., 1990a]. Major features of sampling systems which generated data evaluated in this study are summarized in Table 1. The University of Virginia (UVA) and the Air Quality Group (AQG; now referred to as the Aerosol Research Section) from the National Oceanic and Atmospheric Administration (NOAA) sampled the western NAO boundary layer (BL) and free troposphere (FT) with a high-flow dichotomous filter pack system mounted on the NOAA King Air research aircraft [Bardwell et al., 1990]. Air was sampled within 250 km of the U.S. mid-Atlantic coast and in the vicinity of Bermuda.

Atmospheric samples were also collected with a variety of systems throughout the NAO from a 10-m bow tower on the NOAA ship Mt. Mitchell. UVA/AQG sampled major particulate- and vapor-phase species with a bulk filter pack system similar in design and operation to the bulk filter pack component of the dichotomous system deployed on the aircraft [Bardwell et al., 1990]. Intercomparison with data from other measurement systems on the ship indicates that the open-face inlet on this shipboard sampler selectively excluded larger particles resulting in an approximate 20% underestimate of sea-salt species.

NOAA's Atlantic Oceanographic and Meteorological Laboratory (AOML) sampled BL air from the ship with a filter pack system, a high-volume aerosol sampler (hivol), and a six-stage cascade impactor [Pszenny et al., 1990b]. In addition, the University of Rhode Island (URI) sampled atmospheric aerosol with a seven-stage cascade impactor [Pszenny et al., 1989]. The AOML filter pack was designed to sample fine aerosol and alkaline reactive N and S gases preferentially. Intercomparison with other data sets for shipboard collections suggests that the inlet for this sampler selectively excluded approximately two thirds of the sea-salt aerosol mass. Relationships between wind velocity and sea-salt aerosol concentrations measured with the AOML hivol were similar to those observed some years ago in the NAO with an isokinetic sampler [Lovett, 1978] suggesting that the hivol collected representative samples of sea-salt aerosol mass.

A number of potential artifacts could bias data for size-segregated aerosol generated with cascade impactors in marine regions. These include internal losses on slot throats of 25% to 30% [Willeke, 1975], significant retention of HCl by Whatman 41 substrates for contact times longer that about 1 ms [Fogg, 1986], and inefficient retention of submicron aerosol by Whatman 41 backup filters [Lodge, 1986]. Although internal losses may have introduced modest negative bias for impactor data reported in this paper, other artifacts were probably not important. Calculated contact times for the cascade samplers were typically less than 1 ms, suggesting that retention of HCl, and by analogy HNO_3, was probably minimal under our sampling conditions. In addition, a large body of information indicates that Whatman 41 filters collect representative samples of submicron aerosol [e.g., Lowenthal and Rahn, 1987; Watts et al., 1987; Kitto and Anderson, 1988].

The qualities of most data sets evaluated in this study have been assessed by thorough in-house testing and by intercomparison [e.g., Bardwell et al., 1990; Boatman et al., 1990; Pszenny et al., 1990b]. There were, however, no independent measurements of HCl by other groups to intercompare with measurements by UVA and AQG. Given this lack of independent information, and in light of the importance of these data for the present study, we include in the appendix a brief assessment for the quality of HCl and non-sea-salt (nss) Cl^- data generated during the experiment. Results indicate that particle-to-particle and gas-to-particle reactions on bulk aerosol prefilters may cause large (factor of 2) positive bias in measurement of HCl and negative bias in measurement of particulate nss Cl^-. As such, we recommend that published data for these species which were generated using bulk prefilters be viewed with caution.

TABLE 1. Sampling

Organization	Sampling: Technique	Sampling: Media	Sampling: Mean Rate, m^3 STP min^{-1}	Size Fractions	Aerodynamic Cut Radii, μm
UVA/AQG	dichotomous filter pack	aerosol: 90-mm quartz filter (Pallflex QAT-UP 2500) gas: 90-mm rayon filter (Schleicher and Schuell 8S) impregnated with 0.1 M K_2CO_3 in 10% glycerol	0.29 (bulk) 0.10 (fine)	2[b]	0.4
	bulk filter pack	same as above	0.30	1	N.A.
AOML	bulk filter pack	aerosol: 47-mm quartz filter (Pallflex QAT-UP 2500) gas: 47-mm rayon filter (Schleicher and Schuell 8S) impregnated with 0.1 M K_2CO_3 in 10% glycerol	0.085	1	N.A.
	hivol bulk aerosol sampler	20 x 24-cm cellulose filter (Whatman 41)	1.3	1	N.A.
	hivol cascade impactor (Sierra Model 235)	cellulose filter (Whatman 41)	1.1	6	3.6, 1.5, 0.75, 0.45, 0.26, <0.26
URI	hivol cascade impactor (Modified Sierra Model 235)	frosted polycarbonate impaction substrates [Pszenny et al., 1989] final quartz filter (Whatman QMA)	1.1	7	8.4, 4.2, 1.8, 1.0, 0.48, 0.26, <0.26

Abbreviations are as follows: UVA, University of Virginia; AQG, NOAA Air Quality Group; AOML, NOAA Atlantic Oceanographic and Meteorological Laboratory; URI, University of Rhode Island; FT, free troposphere; BL, boundary layer; N.A., not applicable.

Systems

Species Measured[a]		Average Deployment Time, hours	Platform	Cruise Leg	Number of Samples
Aerosols	Gases				
SO_4^{2-}, NO_3^-, Cl^-, $CH_3SO_3^-$, $HCOO_t$, CH_3COO_t, NH_4^+, Na^+, Mg^{2+}, K^+, Ca^{2+}	SO_2, HNO_3, HCl	1.5 (FT)[b] 0.8 (BL)[b]	aircraft	1	8 (FT) 16 (BL)
same as above	same as above	1.0	ship	1	20
SO_4^{2-}, NO_3^-, Cl^-, $CH_3SO_3^-$, NH_4^+, Na^+, Mg^{2+}, K^+, Ca^{2+}	SO_2, HNO_3	11.4	ship	1 2 3 4	22 15 11 21
same as above	N.A.	26.3	ship	1 2 3 4	10 5 3 6
same as above	N.A.	32.7	ship	1 3 4	1 3 2
same as above	N.A.	71.5	ship	3 4	

[a] SO_4^{2-}, NO_3^-, Cl^-, $CH_3SO_3^-$, $HCOO_t$, CH_3COO_t, SO_2, and HNO_3 were analyzed by ion chromatography. NH_4^+ was analyzed by automated colorimetry. Na^+, Mg^{2+}, K^+, and Ca^{2+} were analyzed by flame absorption spectrometry.

[b] Bulk and fine filter packs were deployed in the boundary layer; only bulk filter packs were deployed in the free troposphere.

3. RESULTS AND DISCUSSION

3.1. Distributions of HCl in the Western NAO Troposphere

The vertical distributions of HCl measured near the U.S. east coast and in the vicinity of Bermuda are summarized in Figure 1. Given uncertainties in the quality of the various data sets, HCl estimated from collections for bulk and fine filter packs are depicted separately. Concentrations of sea salt in the FT were below detection limits, and it is therefore unlikely that reactions involving sea salt were a major source of bias for these higher altitude measurements of HCl using bulk filter pack samplers. In light of the assessment of data quality (see appendix), we believe that distributions of ambient concentrations of HCl in the lower BL (altitude 152 m) are probably best represented by the lower concentrations measured with the fine filter packs on the aircraft. Near-surface measurements using bulk filter packs aboard the ship may have overestimated ambient concentrations by a factor of approximately 2.

The observed distributions of concentrations (Figure 1) indicate marked vertical and horizontal variability. Concentrations of HCl were highest near the surface and decreased rapidly with altitude. This distribution parallels the vertical distribution of sea-salt aerosol (Table 2). Concentrations of HCl near the east coast were approximately 2 times greater at all altitudes relative to corresponding values near Bermuda. With the exception of shipboard measurements on July 22, all concentrations greater than 0.75 ppbv were observed on the first day of sampling when large anthropogenic influences were evident (see companion papers in this issue). The unusually high (greater than 1 ppbv) HCl concentrations observed on July 22 were also associated with anthropogenic emissions. Ship observations coupled with trajectory analyses and measurements of ^{222}Rn and graphitic carbon indicate that heavy ship traffic in the vicinity of the research vessel significantly impacted the local atmosphere [Hansen et al., 1990]. Like the situation in the immediate vicinity of the east coast, combustion products were associated

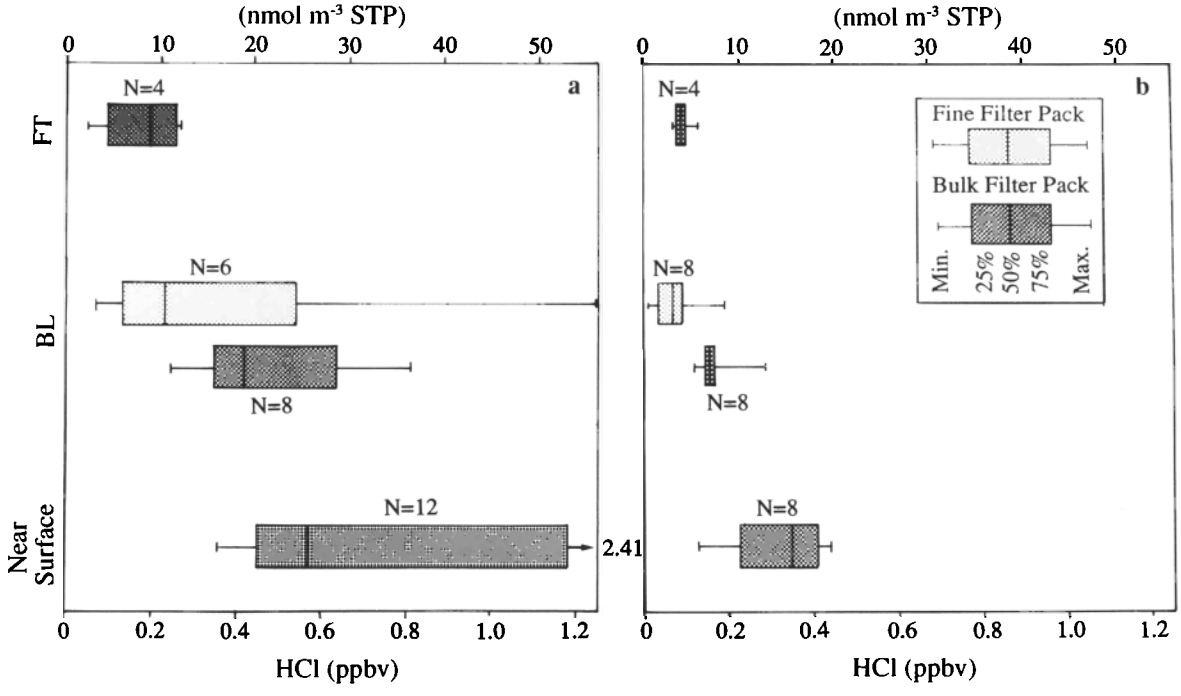

Fig. 1. Distributions of HCl (a) near the east coast and (b) near Bermuda measured with the UVA/AQG filter pack samplers on the ship (indicated as near surface) and on the aircraft in the boundary layer (BL) (152 m) and in the free troposphere (FT) (1676-2591 m). Data for fine and bulk filter packs are depicted separately.

TABLE 2. Cl^- Loss From the Particulate Phase

Date (DDMM)	Ship: Mid Time, UT	Ship: Particulate Cl^- ±SE, nmol m^{-3} STP	Ship: Particulate Cl^- Deficit ±SE, nmol m^{-3} STP	Ship: Loss, %	Aircraft (BL): Mid Time, UT	Aircraft (BL): Particulate Cl^- ±SE, nmol m^{-3} STP	Aircraft (BL): Particulate Cl^- Deficit ±SE, nmol m^{-3} STP	Aircraft (BL): Loss, %
			East Coast					
17/07	1502	17.5±2.2	125±13.6	88	1604	6.8±1.8	<31.9	...
	1615	55.5±2.1	89.5±13.3	62	1702	<4.9	<44.1	...
18/07	1508	175±2.1	<26.6	...	1534	37.8±1.9	<34.1	...
	1632	141±2.2	<27.3	...	1631	7.7±2.8	<49.1	...
19/07	1506	147±2.1	<26.0	...	1638	12.6±1.8	<31.7	...
	1621	124±2.1	<25.8	...	1737	5.0±1.8	41.5±16.0	89
20/07	1721	153±2.0	<25.6	...				
	1844	158±2.2	<27.2	...				
21/07	1507	145±2.0	<24.4	...	1510	14.5±1.8	50.9±16.4	78
	1620	174±1.9	<24.0	...	1610	13.2±1.8	<31.7	...
22/07	1633	32.5±2.1	70.7±13.4	69				
	1804	44.5±2.2	51.7±13.7	54				
Average		114	31.4	22[a]		12.6	22.2	64[a]
			Bermuda					
25/07	1505	36.2±2.2	<27.2	...				
	1609	40.9±2.2	37.4±13.8	48				
26/07	1321	67.5±2.4	<28.0	...	1422	5.6±1.6	<54.2	...
	1457	56.3±2.6	<31.9	...	1528	4.7±1.5	<54.2	...
27/07	1012[b]	30.1±0.5	15.1± 1.6	33				
	1245	38.9±2.2	41.6±14.3	52	1220	<3.2	<56.3	...
	1431	34.0±2.3	<28.2	...	1321	4.2±1.5	<53.0	...
	2008	11.1±2.2	<27.0	...	1933	3.9±1.6	<54.8	...
	2138	22.2±2.2	<27.6	...	2033	3.3±1.6	<53.6	...
28/07					1346	<3.2	<55.2	...
					1446	4.0±1.5	<53.0	...
Average		37.4	19.2	34[a]		3.7	9.6	72[a]
			Leg 3					
18/08	0803[c]	113±3.4	34.5±4.3	23				
21/08	1705[b]	36.2±0.6	43.0±1.9	54				
22/08	0800[c]	49.3±1.4	39.9±2.7	45				
Average		66.3	39.1	37[a]				
			Leg 4					
28/08	0830[c]	82.8±1.1	16.9±3.0	17				
29/08	2040[b]	249±3.5	77.8±9.9	24				
31/08	0835[c]	248±1.9	48.0±8.8	16				
01/09	1438[b]	52.1±0.6	11.5±1.8	18				
02/09	2058[c]	40.7±0.6	6.6±1.5	14				
03/09	0855[b]	37.0±0.4	9.0±1.3	20				

TABLE 2. (continued)

Date (DDMM)	Ship: Mid Time, UT	Ship: Particulate Cl^- ±SE, nmol m^{-3} STP	Ship: Particulate Cl^- Deficit ±SE, nmol m^{-3} STP	Ship: Loss, %	Aircraft (BL): Mid Time, UT	Aircraft (BL): Particulate Cl^- ±SE, nmol m^{-3} STP	Aircraft (BL): Particulate Cl^- Deficit ±SE, nmol m^{-3} STP	Aircraft (BL): Loss, %
			Leg 4 (continued)					
05/09	0322[c]	40.8±1.1	-7.8±1.1	-16				
05/09	1524[b]	21.4±0.3	8.6±1.1	29				
Average		96.5	21.3	18[a]				

Unless otherwise noted, shipboard data correspond to samples from the UVA/AQG bulk filter pack. SE, standard error.

[a]Average percent losses are calculated from average concentrations of particulate Cl^- and average Cl^- deficits for the specified data sets. Individual measurements below detection limits were included in the calculation of average concentrations.

[b]Sum of concentrations for stages 1 through 4 of AOML cascade impactor.

[c]Sum of concentrations for stages 0 through 4 of URI cascade impactor.

with elevated concentrations of HCl and proportionate losses of particulate Cl^- from the sea-salt aerosol (see next section).

3.2. Relationships Between Particulate nss Cl^- and HCl

Virtually all concentrations of particulate nss Cl^- measured from the aircraft in the BL were below system detection limits, thereby precluding a direct comparison with HCl. An initial inspection of data generated with the UVA/AQG sampler on the ship indicates reasonably good agreement between the paired observations and a 1 to -1 line (Figure 2). Similar correlations between HCl and nss Cl^- have been reported previously for marine air masses in California [Wall et al., 1988]. Observations from both of these investigations are consistent with the hypotheses that sea-salt aerosol is the primary source for HCl in the marine BL and that HCl and sea-salt aerosol have similar atmospheric lifetimes against deposition, as was suggested by Kritz and Rancher [1980].

Distinct patterns become evident when the paired data are partitioned into subgroups based on chemical and meteorological analyses. Four samples were collected on July 17 and 22 in air masses exhibiting significant anthropogenic influences (Figure 2, solid squares). Within analytical uncertainties, the concentrations of HCl measured during these periods were directly proportional to the corresponding Cl^- deficits for the particulate phase. Similarly, six of eight paired measurements in the vicinity of Bermuda (Figure 2, open circles) indicate direct proportionality between HCl and Cl^- deficits. In contrast, eight data pairs for cleaner maritime air sampled near the east coast (Figure 2, solid circles) exhibited consistently higher concentrations of HCl relative to Cl^- deficits. The ratio of arithmetic averages is 4.5 to 1.0. We recognize that all of these nss Cl^- concentrations were below analytical detection limits, but the consistency of the pattern cannot be dismissed on this basis alone. If the data are unbiased, and if real proportionality exists in the ambient BL, these paired measurements would be distributed around the 1 to -1 line. Assuming that HCl does originate with sea-salt aerosol, these data suggest that the atmospheric lifetime of HCl against deposition may be considerably longer than that of sea-salt aerosol in southeasterly maritime flow near the U.S. east coast during the summer. This is not an unexpected result given the relatively high concentrations of sea-salt aerosol observed during this period (Table 2). Such concentrations would be associated with larger median particle sizes and greater deposition velocities for sea-salt

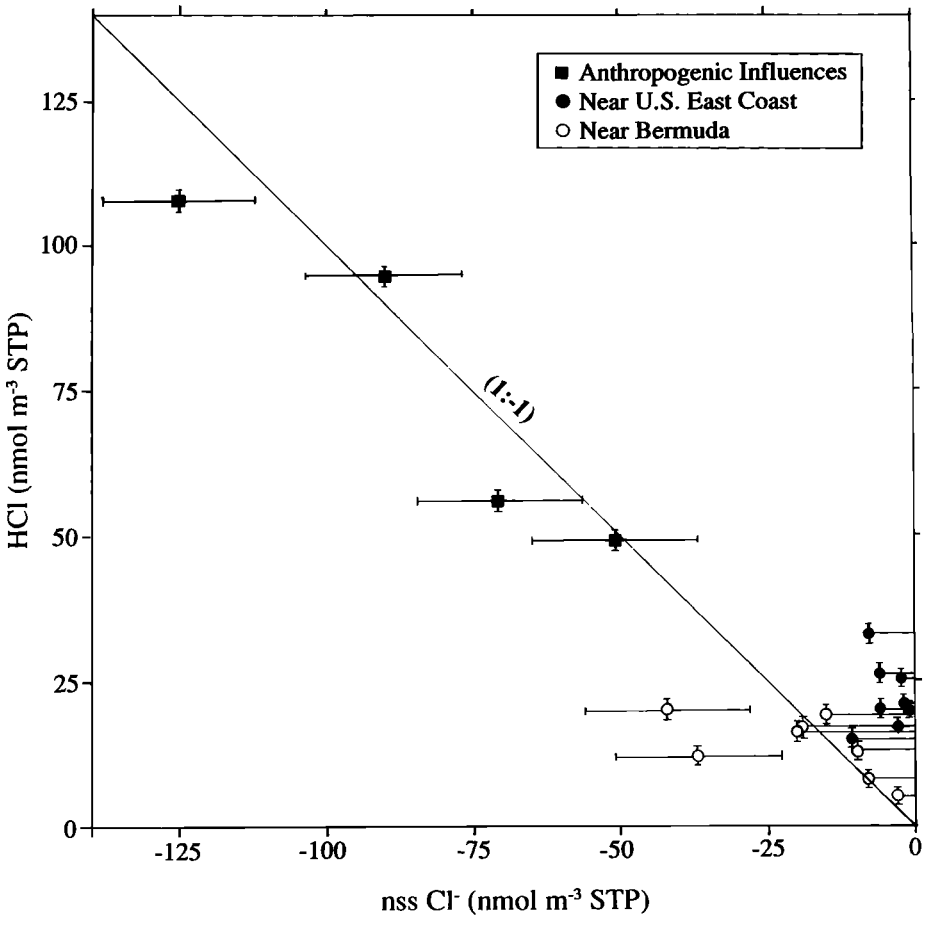

Fig. 2. Comparison between HCl and nss Cl^- measured simultaneously with the UVA/AQG bulk filter pack sampler on the ship.

aerosol relative to most other periods during the cruise.

The analysis presented above suggests that the atmospheric lifetime of HCl against deposition may be longer than that of sea-salt aerosol in some marine air-masses. The presence of a possible artifact (see appendix) which may have caused overestimates of ambient HCl and Cl^- deficits does not seriously compromise the above assessment, since both constituents should be affected equally. The absolute magnitudes of the observed relationships would, however, be impacted by such an artifact.

3.3. Magnitude of Cl^- Loss From the Particulate Phase

The magnitudes of Cl^- deficits observed for data generated with the UVA/AQG filter packs on the aircraft and the ship and with the AOML and URI cascade impactors on the ship are summarized in Table 2. Data for the AOML filter packs were excluded because the inlet discriminated against large particles, resulting in large underestimates of sea-salt aerosol mass (see section 2). Data for the AOML hivol were also excluded because we expect that larger pressure drops and higher sample loadings contributed to larger artifacts relative to the UVA/AQG filter packs. We emphasize that nss Cl^- data generated with the bulk filter packs are likely to be biased and should be considered as upper limits for actual Cl losses.

Large anthropogenic influences observed on July 17 and 22 were associated with higher absolute and percentage Cl^- deficits relative to other samples collected from the ship near the east coast. Between 54 and 88% of sea-salt Cl^- was lost from near-surface aerosol during these

episodes. From July 19 to 22, relatively clean maritime air was sampled from the ship [Stunder et al., 1990; Hansen et al., 1990]. Some of the highest sea-salt concentrations (Table 2) and lowest Cl^- deficits (average = 6.1 nmol m^{-3} STP; N = 6) observed during the cruise were associated with these conditions. Resolution for nss Cl^- from the aircraft was limited, but mean values near the east coast indicate that the absolute concentrations of Cl^- (22.2 nmol m^{-3} STP) lost from sea-salt aerosol at 152 m were similar to those lost from near surface aerosol (31.4 nmol m^{-3} STP). Large differences in the percentages lost result in part from relatively lower absolute concentrations of sea salt at the higher altitude (Table 2). If there is a significant time dependence on the magnitude of Cl^- release, the older average age of sea-salt aerosols at higher altitude may contribute to larger percentage deficits observed in aircraft samples.

Relative to the east coast, lower concentrations of sea-salt aerosol and Cl^- deficits were measured from the ship near Bermuda. Average values for aircraft samples suggest that major features of the vertical distributions near Bermuda were similar to those observed near the east coast. Concentrations of sea-salt aerosol decreased, and percentages of Cl^- lost from the aerosol increased with altitude.

The highest average Cl^- deficits (39.1 nmol m^{-3} STP) and percentage losses (37%) were observed from the ship during leg 3 between Iceland and the Azores. Trajectory classifications based on the origin of airmasses [Stunder et al., 1990] suggest that anthropogenic sources are probably not related directly to the observed losses of Cl^- during these sampling periods. Relative to other legs of the cruise, high concentrations of sea salt, low Cl^- deficits and low percentage losses were observed during leg 4 (Table 2). Assuming that the Cl^- lost from sea-salt aerosol generated equivalent concentrations of HCl and that the lifetime of HCl in the BL is at least as long as that of sea-salt aerosol, the Cl^- deficits measured on legs 3 and 4 correspond to minimum mean estimates for HCl of 0.9 ppbv and 0.5 ppbv, respectively.

3.4. Assessment of Hypothesized Mechanisms for Cl^- Loss From Particles

The two major hypothesized mechanisms by which Cl^- is released from sea-salt aerosol involve acid-base desorption (reactions (1) and (2)), and reactions between nonacidic N gases and sea-salt aerosol (reactions (3), (4), and (5)). If acid-base reactions were the principal mechanism of release, Cl^- deficits in coarse fractions of aerosols would be less than the corresponding sums of anions from H_2SO_4 and HNO_3 because the aerosol, which is initially alkaline, must first be acidified before desorption can occur [Brimblecombe and Clegg, 1988]. Taking account also of acid neutralization by NH_3, this relationship can be expressed on an equivalence basis as follows:

$$[-\text{nss } Cl^-] < ([\text{nss } SO_4^{2-}]+[NO_3^-]-[NH_4^+]) \quad (6)$$

If the alternative hypothesis involving nonacidic N gases were the primary mechanism of release, then Cl^- deficits in coarse fractions would equal those of coarse particulate NO_3^- as follows:

$$[-\text{nss } Cl^-] = [NO_3^-] \quad (7)$$

Each of these relationships represents a maximum estimate for the amount of Cl desorbed by the corresponding mechanism, since neither is mutually exclusive of the other.

Relationships (6) and (7) were evaluated with both the AOML and URI data sets for the cascade impactors (Figure 3a). Eleven of the 12 samples revealed losses of Cl^- from the particulate phase (i.e., positive Cl^- deficits). Results of the Wilcoxon Signed Ranks Test indicate that Cl^- deficits in coarse fractions (greater than 50% aerodynamic cut radius of 0.5 μm) were significantly greater (alpha=0.05) than both the concentrations of anions from unneutralized H_2SO_4 and HNO_3 in the coarse mode and the concentrations of coarse NO_3^-. Acid-base desorption reactions could account for maxima of between less than 1 and 57% of Cl released from the particulate phase. Reactions involving N gases (including HNO_3) and sea-salt aerosol could account for maxima of between 4 and 47% of the Cl^- loss. Minima of between 43 and 96% of observed Cl^- deficits could not be accounted for by the combined effect of these major hypothesized mechanisms. We note here that similar relationships among the products of reactions (1) through (5) were observed over the tropical Pacific Ocean between 85°W and 180° longitude during a January-February 1990 shipboard study conducted by the NOAA AOML (A. A. P. Pszenny, unpub-

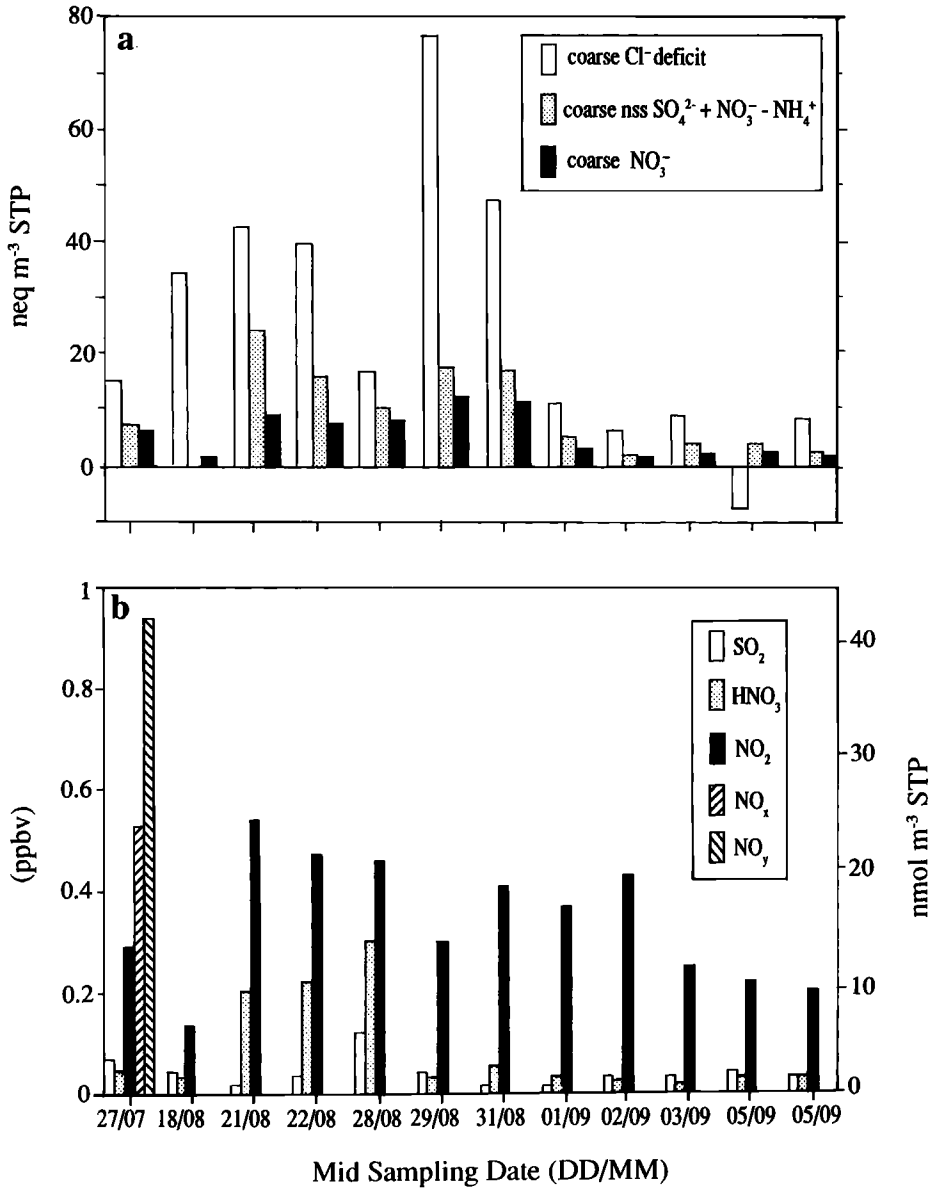

Fig. 3. (a) Comparisons among the sums of Cl^- deficits, anions from strong acids (approximated as nss $SO_4^{2-} + NO_3^- - NH_4^+$), and NO_3^- in the coarse stages of AOML (1 through 4) and URI (0 through 4) cascade impactors operated on the ship, and (b) corresponding concentrations of SO_2 and odd N gases measured on the ship during overlapping but not entirely concurrent sampling periods. SO_2 and HNO_3 were measured with the AOML filter pack sampler. NO_2, NO_x, and NO_y data were provided by D. Hastie (personal communication, 1990). (See Hastie et al. [1990] for methodological details).

lished data, 1990). These new observations indicate that the implications of our analysis are not restricted to the NAO but may apply to the marine BL on a global scale.

Concentrations of potential reactant and product gases were averaged over each sampling interval for the cascade impactors and are plotted in Figure 3b. Because of the possibility for artifacts

resulting from gas-to-particle reactions on bulk prefilters (see appendix), SO_2 and HNO_3 concentrations measured with the AOML filter pack are considered lower estimates. The highest concentrations of NO_3^- and four of the five highest Cl^- deficits measured on coarse impactor stages were observed for the five samples collected between August 21 and 31. The first three of these samples corresponded to the three highest mean HNO_3 concentrations measured during impactor sampling. The other two samples were collected during the period of highest sea-salt concentrations encountered during the cruise (Table 2). Significant concentrations of Saharan dust were also apparent in conjunction with these two samples. Higher concentrations of sea-salt aerosol would be expected to scavenge HNO_3 more efficiently from the ambient BL, causing a shift in partitioning toward the particulate phase. The decrease in HNO_3 between August 28 and 29 (11.6 nmol m^{-3} STP) is in the range of the observed increase in coarse NO_3^- (4.4 nmol m^{-3} STP). By comparison, the Cl^- deficit in coarse fractions increased by 60.9 nmol m^{-3} STP over the same period, indicating that only a minor fraction of the volatilized Cl could be explained by increased scavenging of HNO_3. The average concentrations of NO_2 during impactor sampling intervals were less variable relative to HNO_3 and coarse particulate NO_3^- [Hastie et al., 1990]. There were no obvious relationships between NO_2 and Cl^- deficits in coarse fractions. NO_x and NO_y data were available for only the first cascade impactor sampling period.

Mean concentrations of SO_2 for 11 of the 12 sampling intervals were less than 2.7 nmol m^{-3} STP. These concentrations were similar to those for nss SO_4^{2-} which averaged 2.8 nmol m^{-3} STP in the coarse fractions of all samples. Considering the short atmospheric lifetime of sea-salt aerosol [e.g., Kritz and Rancher, 1980], these measurements of SO_2 and coarse-fraction nss SO_4^{2-} suggest that SO_2 has a short lifetime in the marine BL against scavenging by sea-salt aerosol (also see Sievering et al. [1991]). If sufficient acidity is present to lower the aerosol pH below 3.0, HCl volatilization would be expected from reaction (2) [Brimblecombe and Clegg, 1988].

The large Cl^- deficits observed in the impactor data were not balanced on an equivalent basis by measured anions. These results suggest the possibility that Na^+ was systematically overestimated, or that Cl^-, NO_3^-, or SO_4^{2-} were systematically underestimated, by large factors. Quality assurance assessments indicate, however, that such large errors were unlikely. Two sets of spike recovery tests for major seawater species were performed in the laboratory at AOML on both Whatman 41 and Pallflex quartz filters. The results of one experiment indicated an approximate 90% recovery of SO_4^{2-}, and both experiments indicated Mg^{2+} recoveries of only 80 to 90% from Whatman 41 filters. Otherwise, all ions were recovered from both filter types with efficiencies not significantly different from 100%. Additional experiments are planned to confirm whether SO_4^{2-} recoveries from Whatman 41 are indeed significantly less than 100%, but the magnitude of possible bias from incomplete recovery is small relative to the concentrations of missing anions in samples.

Alternatively, unmeasured anions may be important chemical constituents of coarse marine aerosol fractions. HCO_3^- is one possibility, but estimation of $[HCO_3^-]$ is precluded by lack of reliable H^+ measurements for the cascade impactor samples. Few experimental investigations of the acid-base chemistry of coarse sea-salt aerosol have been conducted. On the basis of limited data [e.g., Winkler, 1980, 1986], however, it appears that the pH of sea-salt aerosol is typically in the range of 7.0 to 9.0. This implies that HCO_3^- may contribute significantly to the ionic strength of sea-salt aerosol and, if so, may represent the missing anions in our samples. If this is the case, it has important implications for the mechanism by which Cl is released from the aerosol. Essentially no HCl will volatilize directly from sea-salt aerosol in this pH range. Indeed, neutral or alkaline aerosol would represent a net sink for atmospheric HCl. If sea-salt aerosol does scavenge HCl from the atmosphere, then the release rates of other volatile Cl compounds from the aerosol would be greater than those inferred from measured Cl^- deficits, for which a conservative Cl source based on the seawater ratio with Na^+ is assumed. This point is discussed in section 4.

In summary, the analysis presented above does not provide clear evidence supporting either of the major hypothesized mechanisms by which Cl is released from sea-salt aerosol, although such reactions are not precluded by our observations. Our measurements of the products

of reactions (1) through (5) indicate, however, that an average of only 38% of the measured Cl^- lost from the particles could be accounted for by these mechanisms. This suggests that other processes may be occurring that also lead to Cl loss from sea-salt aerosol.

3.5. A Photochemical Cl^- Loss Mechanism

Petriconi and Papee [1972] observed the volatilization of Cl^i_g and NO_x from concentrated seawater-$NaNO_3$ solutions irradiated with natural sunlight under ambient air conditions. Ionic strengths and concentrations in the solutions were similar to those expected for natural sea-salt aerosols in the marine BL [Brimblecombe and Clegg, 1988]. The rate of Cl^i_g volatilization increased with increasing $NaNO_3$ concentrations, suggesting a radical mechanism initiated by photolytic reduction of NO_3^- [Zafiriou and True, 1979]. Significant Cl^i_g volatilization was still observed in the absence of $NaNO_3$, however, and was attributed by Petriconi and Papee [1972] to an alternate Cl^- oxidation mechanism initiated by photolysis of O_3 in the ambient air. Recently, smog chamber experiments by Zetzsch et al. [1988] and Behnke and Zetzsch [1989] have documented the production of Cl_2 from irradiation of moist artificial NaCl aerosols in the presence of O_3. The production of Cl_2 was also observed in the dark but was slower.

Behnke and Zetzsch [1989] proposed that the production of Cl_2 in their experiments resulted from oxidation of Cl^- by $^{\cdot}OH_{(aq)}$ [Jayson et al., 1973; McElroy, 1990], where $^{\cdot}OH_{(aq)}$ can be generated in a number of ways following photolysis of O_3 [Chameides and Davis, 1982; Jacob, 1986]. For example,

$$O_{3(g)} + h\nu \longrightarrow O_{2(g)} + O(^1D)_{(g)} \quad (8)$$

$$O(^1D)_{(g)} + H_2O_{(g)} \longrightarrow 2\ ^{\cdot}OH_{(g)} \quad (9)$$

$$^{\cdot}OH_{(g)} \longrightarrow {}^{\cdot}OH_{(aq)} \quad (10)$$

$$^{\cdot}OH_{(aq)} + Cl^- \longrightarrow {}^{\cdot}ClOH^- \quad (11)$$

$$^{\cdot}ClOH^- \longleftrightarrow Cl^{\cdot}_{(aq)} + OH^- \quad (12)$$

$$Cl^{\cdot}_{(aq)} + Cl^- \longleftrightarrow {}^{\cdot}Cl_2^- \quad (13)$$

$$^{\cdot}Cl_2^- + {}^{\cdot}Cl_2^- \longrightarrow Cl_{2(g)} + 2\ Cl^- \quad (14)$$

The recombination of $^{\cdot}Cl_2^-$ is quenched in dilute solutions because of $Cl^{\cdot}_{(aq)}$ hydrolysis [McElroy, 1990], but it may be efficient in concentrated solutions where the $Cl^{\cdot}_{(aq)}/{}^{\cdot}Cl_2^-$ equilibrium (reaction (13)) is shifted toward $^{\cdot}Cl_2^-$. The mechanism (8)-(14) implies an increase in Cl_2 production with increasing acidity, due to (12), which is consistent with the pH dependence of Cl^i_g release observed by Petriconi and Papee [1972].

A photolytic source of $^{\cdot}OH_{(aq)}$ cannot, however, explain the production of Cl_2 observed by Behnke and Zetzsch [1989] in the dark. Possibly, $^{\cdot}OH_{(aq)}$ could be produced by reactions of O_3 at electron donor sites on the aerosol surface [Heikes, 1984]. Alternatively, direct surface reaction of O_3 with Cl^- may occur [Behnke and Zetzsch, 1989]:

$$2\ Cl^- + O_{3(p)} \xrightarrow{H_2O} Cl_{2(g)} + 2\ OH^- + O_{2(g)} \quad (15)$$

Note that the stoichiometry of (15) is the same as that of the ensemble of (8)-(14). Both involve the loss of one O_3 molecule per Cl_2 molecule produced, and both involve production of alkalinity. HCO_3^- would replace the Cl^- lost from the sea-salt aerosol, thus accounting for the missing anions in our samples (see section 3.4).

3.6. Geochemical Cycling of Reactive Cl in the Marine BL

Losses of particulate Cl^- observed during GCE/CASE/WATOX include typically 10 nmol m^{-3} STP (0.25 ppbv), at minimum, which could not be attributed to acid displacement reactions. Following section 3.5, we assume as a working hypothesis that these losses reflect the volatilization of Cl_2 by a mechanism with the stoichiometry of (15). Photolysis of Cl_2 in the daytime takes place on a time scale of minutes and produces Cl$^{\cdot}$, which reacts rapidly to yield HCl and $ClNO_3$ (the latter via ClO). As was discussed in section 3.4, the low concentrations of coarse particulate NO_3^- (Figure 3) suggest that reactions involving $ClNO_3$ are probably of minor importance. HCl is scavenged efficiently by aerosol [Watson et al., 1990], closing the Cl cycle (Figure 4). We estimate a time scale of the order of 10 min for scavenging of HCl by sea-salt aerosol in surface air based on a calculation of gas-to-aerosol fluxes [Fuchs and Sutugin, 1971] and, assuming negligible vapor, a sticking coefficient of 0.15 [Watson et

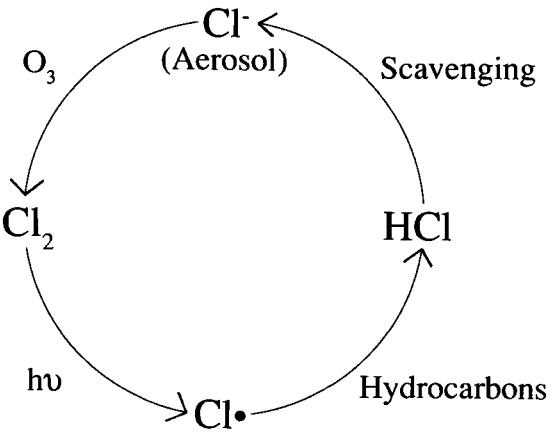

Fig. 4. Hypothesized geochemical cycle of reactive inorganic chlorine in the marine boundary layer.

al., 1990], and a sea-salt aerosol mass concentration of 10 μg m^{-3} [Pszenny et al., 1990b] with typical Junge-size distribution in the 0.1- to 10-μm radius range [Parungo et al., 1986]. We note that the scavenged HCl would neutralize alkalinity generated via reaction (15), indicating that this sequence of chemical transformations is self-regulating with respect to the acid-base balance of sea-salt aerosol. Steady state between Cl_2 volatilization from the aerosol and scavenging of HCl by the aerosol imply a Cl_2 source of the order of 1 ppbv h^{-1} in the daytime.

From the mechanism described above, one would expect enhanced Cl^- deficits in aerosols at night, when Cl_2 is not photolyzed. Cl^- deficits measured using the AOML filter packs were examined for evidence of diel periodicity. Although data quality evaluations indicate that these nss Cl^- data may be biased (see appendix), there is no reason to expect systematic differences in the relative magnitudes of bias between the daytime and nighttime samples. The data set was partitioned into subsets that included Cl^- deficits measured during three consecutive 12-hour sampling periods (A, B, and C, respectively). The mean deficit for the two nighttime or two daytime samples (A and C) in each subset was then subtracted from the deficit for the middle sample (B) to determine the net difference in desorbed Cl^-. If there was no diel periodicity in Cl^- deficits, the mean of these differences would be approximately 0, and approximately equal numbers of positive and negative values would be observed. The net differences for all available data subsets are plotted in Figure 5a for nighttime samples and in Figure 5b for daytime samples. Cl^- deficits during the night were greater than the corresponding daytime values for 9 of 12 data subsets (Figure 5a). The Wilcoxon Signed Ranks Test indicates that differences between these populations of nighttime and daytime Cl^- deficits were marginally nonsignificant at alpha=0.05. Given the high degree of variability in the data, it is possible the lack of significance simply reflects the small number of paired observations. On average, the nighttime Cl^- deficits for these samples were greater than daytime values by 8.6 nmol m^{-3} STP or 50%. Conversely, Cl^- deficits for daytime samples were less than the corresponding nighttime values for 10 of 13 data subsets (Figure 5b). These differences were significant at alpha=0.05. Average daytime Cl^- deficits for these samples were less than nighttime values by 16.2 nmol m^{-3} STP or 70%. The observed diel periodicity in the net flux of Cl from sea-salt aerosol is consistent with that expected from the proposed mechanism. We note that a similar analysis of day and night samples by Rancher and Kritz [1980] found no such periodicity.

4. IMPLICATIONS FOR MARINE ATMOSPHERIC CHEMISTRY

4.1. General Considerations

Our postulated explanation for the observed Cl^- deficits (i.e., reaction (15) or the stoichiometric equivalent reactions (8)-(14)) would provide a large source of $Cl^\cdot$ to the marine atmosphere. Such a source would in turn have major consequences for the oxidation of hydrocarbons and dimethyl sulfide (DMS), as oxidation of these compounds is typically 1-3 orders of magnitude faster by $Cl^\cdot$ than by $^\cdot OH$. In polluted environments, the increased supply of peroxy radicals from the $Cl^\cdot$ + hydrocarbon reactions would promote photochemical O_3 production. At the low NO_x concentrations usually found in marine atmospheres, however, uptake of O_3 by sea-salt aerosol would provide a net sink for O_3 because photochemical production is inefficient [e.g., Liu et al., 1983]. A challenging hypothesis emerges that the uptake of O_3 by sea-salt aerosol could

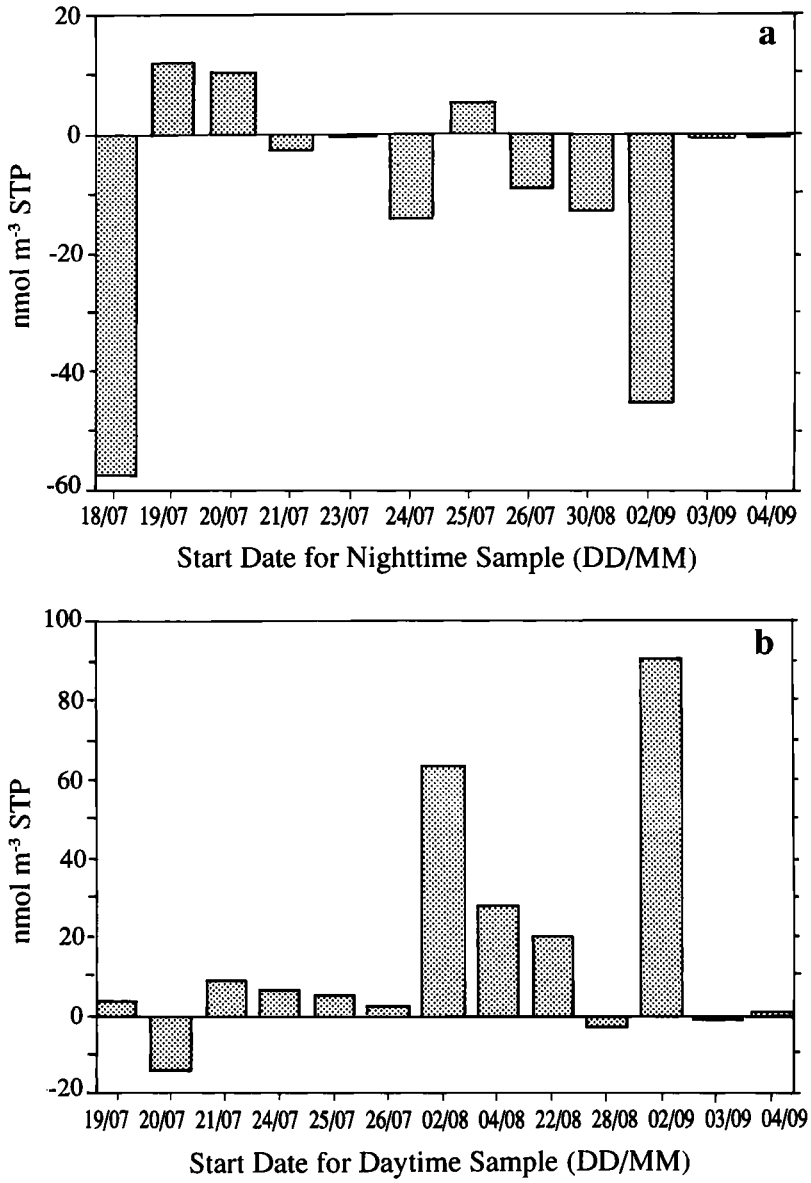

Fig. 5. Diel differences in nss Cl^- measured with the AOML filter pack sampler on the ship. (a) Non-sea-salt Cl^- for nocturnal samples minus the mean nss Cl^- for diurnal samples collected during the preceding and following periods. (b) Non-sea-salt Cl^- for diurnal samples minus the mean nss Cl^- for nocturnal samples collected during the preceding and following periods.

explain the low concentrations of O_3 observed in many ocean regions [Liu et al., 1983; Newell and Wu, 1985; Piotrowicz et al., 1986; 1990; Fishman et al., 1990] and could possibly provide a major global sink for tropospheric O_3.

Concentrations of O_3 measured during GCE/CASE/WATOX are interesting in this respect. Surface concentrations averaged 16 ppbv [Piotrowicz et al., 1990] and increased significantly with altitude [Ray et al., 1990]. Corresponding surface concentrations of $^*NO_x$ (NO_x + peroxyacyl nitrates) averaged 0.3 ppbv [Hastie et al., 1990]. If NO_x accounted for the major portion of $^*NO_x$, as might be

expected at the high temperatures of surface air, then vigorous O_3 production would follow [Lin et al., 1988]. The low O_3 concentrations measured from the ship and from the aircraft in the lower BL (150 m) imply, however, that such production did not occur near the ocean surface. As discussed below, Cl· chemistry may provide the explanation.

4.2. Model Simulations

The sensitivity of atmospheric chemistry to the reactive Cl source represented by reaction (15) was investigated further using 0-D photochemical model simulations of the marine surface air sampled during GCE/CASE/WATOX. The model includes a standard scheme for computing UV radiation intensities [Logan et al., 1981] and a detailed HO_x-NO_x-hydrocarbon chemical mechanism (Lurmann et al. [1986], with modifications by Jacob and Wofsy [1990]). The mechanism was extended to include gas-phase Cl_x reactions [Atkinson and Aschmann, 1985; DeMore et al., 1987; Wallington et al., 1988; Nicovich et al., 1990; Nielsen et al., 1990], and surface reactions of sea-salt aerosol with O_3 (reaction (15)) and $ClNO_3$ (reaction (4)). Rates for the surface reactions are expressed as the gas-to-aerosol fluxes of O_3 and $ClNO_3$, weighted by a ''sticking coefficient'' representing the reactivity of the gas at the surface. The same sea-salt aerosol size distribution is assumed as in section 4.1. An excess surface concentration of Cl^- is assumed, i.e., the reaction rates are not limited by Cl^- availability. A sticking coefficient of unity for $ClNO_3$ is chosen as an upper limit [Finlayson-Pitts et al., 1989]. The sticking coefficient for O_3 is chosen in the range of 10^{-4} to 10^{-3} to generate Cl^- loss rates of the order of 1 ppbv h^{-1} (see section 3.7).

Our first set of simulations considers a closed air parcel in photochemical steady state at noon. Concentrations of $^*NO_x$, O_3, CO, and HCl are fixed at 0.3, 16, 100, and 0.5 ppbv, respectively, on the basis of the GCE/CASE/WATOX data. Concentrations of hydrocarbons, CO, and DMS are fixed on the basis of previous observations in the NAO [Rudolph and Ehhalt, 1981; Marenco and Said, 1989; Andreae et al., 1985]. Concentrations of radicals and secondary hydrocarbons, are assumed to be at chemical steady state and define in particular the partitioning of $^*NO_x$ between NO_x and peroxyacyl nitrates. Steady-state conditions are also assumed for HOCl and Cl_2.

Selected results from five simulations are compared in Table 3. Simulation A includes no Cl· chemistry and is used as reference. Simulations B-E test the effect of various Cl· chemistry schemes. The effect of Cl· production from the HCl + ·OH reaction (simulation B) is limited to a relatively small enhancement in the oxidation rate of alkanes, as was discussed previously by Singh and Kasting [1988]. Perturbations to the HO_x-NO_x-O_3 budgets are negligible because the photochemistry is NO_x-limited. Inclusion of the $ClNO_3$ surface reaction as a source of Cl_2 (simulation C) has no significant effect because the production of ClO (precursor of $ClNO_3$) is inhibited by reactions of Cl· with hydrocarbons. This result is again in harmony with the model calculations of Singh and Kasting [1988], and with our previous assessment that the low concentrations of coarse particulate NO_3^- measured during the experiment suggest that reactions involving $ClNO_3$ were of only minor importance (see section 3.4).

Inclusion of the O_3 reaction at NaCl surfaces (simulations D and E) introduces major perturbations to photochemistry. Oxidation by Cl· becomes a major atmospheric sink for DMS and hydrocarbons. The rapid production of Cl· promotes $ClNO_3$ formation, enhancing the oxidation of $^*NO_x$ to NO_3^- as well as the removal of O_3. The oxidation of alkenes by Cl· generates peroxyacyl radicals, shifting the composition of the $^*NO_x$ pool towards peroxyacyl nitrates relative to simulations A-C. As a result of these two factors, we find in simulation E that photochemical production of O_3 is largely suppressed.

The short lifetime of $^*NO_x$ in simulation E (1.4 hours) seems inconsistent with the high $^*NO_x$ concentrations measured by Hastie et al. [1990] during GCE/CASE/WATOX. This lifetime is computed for surface air conditions, however, and longer lifetimes would be expected at higher altitudes where sea-salt aerosol concentrations are lower [e.g., Blanchard [1983], Table 2). It is possible that $^*NO_x$ from aloft was mixed down and contributed to the higher concentrations measured from the ship. Photolysis of aerosol NO_3^- could also possibly regenerate NO_x [Petriconi and Papee, 1972; Zafiriou and True, 1979]. Alternatively, the higher sticking coefficient for O_3 in

TABLE 3. Model Results for a Surface Air Parcel in Photochemical Equilibrium at Noon

	Simulations				
	A	B	C	D	E
	Concentrations				
$\cdot OH$, x 10^6 cm^{-3}	7.5	7.5	7.5	7.1	4.6
$Cl\cdot$, x 10^3 cm^{-3}		6.1	6.4	130	1100
NO_x,[a] ppbv	0.25	0.25	0.25	0.23	0.14
	Rates of Chemical Production (P) and Loss (L), ppbv h^{-1}				
(P-L) of O_3	1.4	1.4	1.4	1.4	0.14
(P-L) of $^*NO_x$	-0.051	-0.051	-0.053	-0.064	-0.22
L of Cl^-	0	0	<0.001	0.22	2.2
L of $ClNO_3$[b]	0	0	<0.001	0.013	0.17
	Rates of Oxidation by $Cl\cdot$ Relative to those by $\cdot OH$				
DMS	0	0.0009	0.009	0.19	2.7
C_3H_8	0	0.009	0.10	1.97	27
C_3H_6	0	0.008	0.008	0.17	2.4

Simulations are as follows: A, no Cl chemistry; B, gas-phase Cl chemistry only; C, simulation B with surface reaction $ClNO_3 + Cl^-$ added; D, simulation C with surface reaction $O_3 + Cl^-$ added (sticking coefficient of 10^{-4}); E, simulation C with surface reaction $O_3 + Cl^-$ added (sticking coefficient of 10^{-3}).

[a]Computed from the photochemical partitioning of 0.3 ppbv $^*NO_x$ between NO_x and peroxyacyl nitrates (see text).

[b]Including only the uptake at sea-salt aerosol surfaces. Other $ClNO_3$ loss mechanisms are thermal decomposition, photolysis, and reaction with $\cdot OH$.

simulation E (Table 3) may have resulted in overestimates for rates of Cl_2 production.

The diel cycle of $Cl\cdot$ chemistry was examined by integrating the 0-D simulation over 48 hours, starting at midnight. Concentrations of $^*NO_x$, DMS, CO, and primary hydrocarbons are fixed at the same levels as before, while concentrations of other species (including HCl) are allowed to evolve as independent variables. Removal of HCl is regulated by the gas-to-aerosol flux, with a sticking coefficient of 0.15 [Watson et al., 1990]. The sticking coefficient for O_3 is taken as 10^{-3} in the daytime. At night we either use the same value (simulation A') or reduce it to 10^{-5} (simulation B'). The lower sticking coefficient at night is intended to simulate the light dependence of Cl_2 production observed by Behnke and Zetzsch [1989].

Results for HCl, Cl_2, and $Cl\cdot$ concentrations are shown in Figure 6. The sum of HCl and Cl_2 concentrations in the daytime is 0.3–0.5 ppbv, consistent with the observed aerosol Cl^- losses. The higher Cl^- deficits at night (Figure 5) can be explained by nighttime accumulation of Cl_2. Simulation A' indicates a Cl_2 accumulation of 7 ppbv at night, which in reality may be limited by the availability of Cl^- aerosol. The accumulation of Cl_2 to high levels at night, as in simulation A', would produce a surge in $Cl\cdot$ concentrations at sunrise (Figure 6), which would in turn deplete DMS and biogenic hydrocarbons. However, observed DMS concentrations in surface air [Andreae et al., 1985] show no evidence of rapid depletion at sunrise. It appears that nighttime accumulation of Cl_2 must be limited in some way, by either inefficient production or chemical removal. As shown in simulation B', a decrease in the rate of nighttime Cl_2 production can effectively suppress the sunrise surge in $Cl\cdot$ concentrations. Reaction of Cl_2 with DMS [Nielsen et al., 1990] could reduce nighttime Cl_2 levels further.

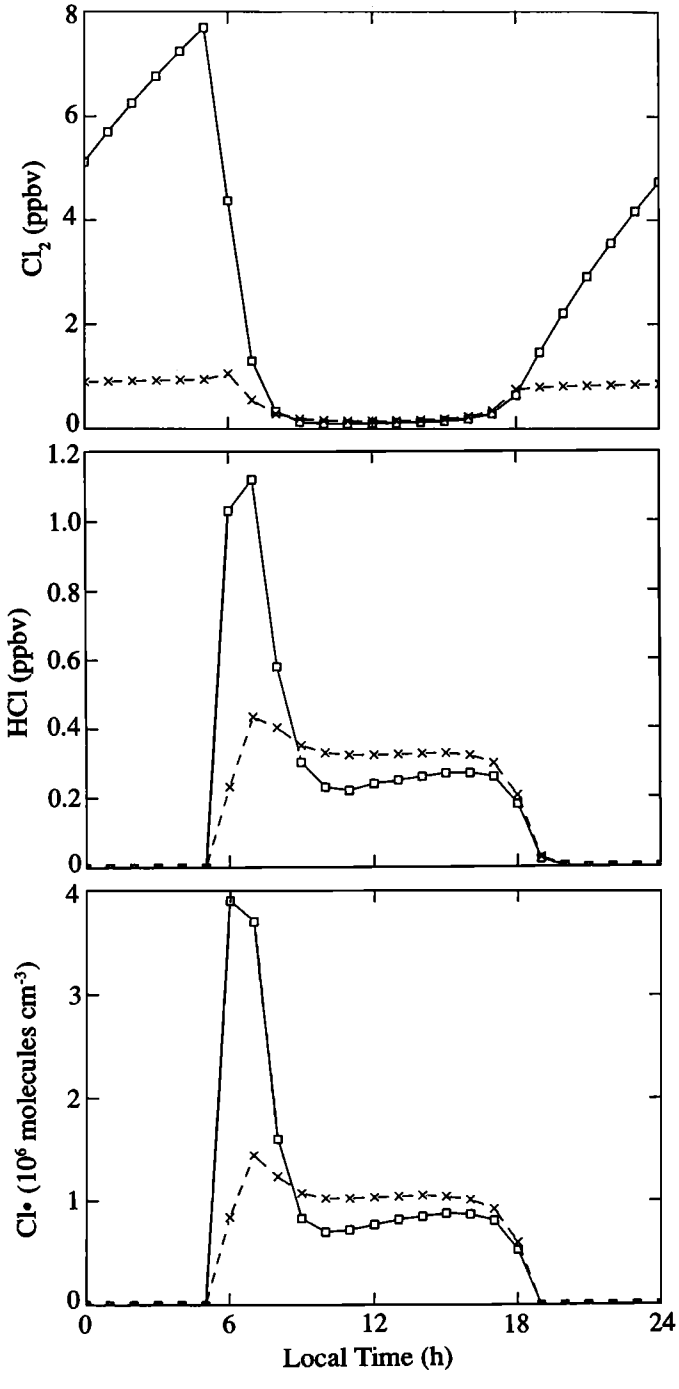

Fig. 6. Simulated concentrations of Cl_2, HCl, and Cl• in marine surface air, as a function of time of day. Model conditions are based on the GCE/CASE/WATOX data. A sticking coefficient of 10^{-3} is assumed for the O_3 reaction at NaCl aerosol surfaces in the daytime. The sticking coefficient at night is assumed identical to that during the day (simulation A'; squares), or is reduced to 10^{-5} (simulation B'; crosses).

5. SUMMARY

Major hypothesized reactant and product species associated with the heterogeneous generation of volatile inorganic Cl from reactions involving sea-salt aerosol in the marine troposphere were measured as a function of phase, particle size, and altitude during the GCE/CASE/WATOX experiment of summer 1988. Air was sampled from the NOAA King Air research aircraft over the western NAO with a dichotomous system which incorporated bulk and fine (50% aerodynamic-cut radius of 0.4 μm) filter packs. Air was also sampled throughout the NAO with two bulk filter pack samplers, a hivol aerosol sampler, and two cascade impactors (six and seven stages) mounted on a 10-m bow tower on the NOAA ship Mt. Mitchell. Data from paired collections with bulk and size-segregated samplers indicate that particle-to-particle and gas-to-particle reactions on bulk aerosol prefilters may cause large (factor of 2) positive artifacts in the measurement of HCl vapor and aerosol Cl^- deficits.

Concentrations of HCl near the surface were typically less than 1.0 ppbv and decreased with altitude and with distance from the U.S. east coast. Concentrations of Cl volatilized from aerosols were generally equivalent to the corresponding concentrations of HCl. Cl^- deficits for the particulate phase ranged from less than detection limits to 125 nmol m^{-3} STP with the highest absolute and percentage losses of Cl typically associated with elevated concentrations of anthropogenic combustion products. Concentrations of product SO_4^{2-} and NO_3^- in coarse fractions of aerosol samples indicate that the combined effect of acid-base desorption and reactions involving N gases (NO_2, $ClNO_3$, N_2O_5, and HNO_3) and sea-salt aerosol could account for maxima of between 4 and 57% of measured Cl^- deficits. This suggests that other processes may be occurring that lead to Cl loss from sea-salt aerosol.

We hypothesize a photochemical mechanism for the Cl loss which involves the reaction of O_3 at NaCl surfaces to generate Cl_2. Rapid photolysis of Cl_2 during the day produces Cl·, which initiates photochemical reactions in an analogous manner to ·OH, yielding HCl. HCl is then scavenged efficiently by the aerosol, closing the Cl cycle. Alkalinity produced by this mechanism would explain anion deficits measured in coarse-fraction aerosol. In addition, the accumulation of Cl_2 during the night that is expected from such a mechanism would explain the significant diel periodicity in the magnitude of Cl^- deficits measured in aerosols during the experiment. Steady state between Cl_2 volatilization from the aerosol and between scavenging of HCl by the aerosol implies a Cl_2 source of the order of 1 ppbv h^{-1} during the day. Uptake of O_3 by sea-salt aerosol may represent an important global sink for tropospheric O_3, contributing to the low concentrations observed in many oceanic regions. Simulations with a 0-D photochemical model suggest that oxidation by Cl· may be a major atmospheric sink for DMS and hydrocarbons. The geochemical cycling of Cl could thus have a significant influence on the oxidative state of the marine troposphere.

APPENDIX: ASSESSMENT OF ARTIFACTS IN HCL AND NSS CL^- DATA

Potential sources of bias in measurements of HCl and nss Cl^- include nonspecificity of the sampling media, volatilization resulting from pressure drops, losses of HCl to inlet or cyclone walls, chemical reactions between different size classes of particles collected in bulk, and chemical reactions between collected particles and gases in the airstream. Alkaline-reactive Cl vapor was sampled quantitatively by the impregnated filters and was measured precisely by our analytical technique [Bardwell et al., 1990]. Previous testing has shown that carbonate impregnated filters selectively exclude organic Cl gases [e.g., Rahn et al., 1976; Berg and Winchester, 1977]. Since HCl is thought to be the principal component of Cl_g^i during the daytime (see, for example, sections 1 and 4.2), large bias in our reported HCl data is not expected as a result of the specificity of the sampling media. HCl was measured only during the day in conjunction with aircraft sampling. In addition, the low pressure drop across the UVA/AQG filter packs [Bardwell et al., 1990] should minimize artifacts resulting from volatilization of particulate Cl^-. Independent information is not available to assess critically the potential loss of HCl to inlet and cyclone walls.

The mixture of coarse (predominantly sea salt) and fine (predominantly sulfur) aerosol on a single filter may generate artifact HCl and Cl^- deficits via reactions (1) and (2) [e.g., Berg and Winchester, 1977; Perdue and Beck, 1988]. Two

sets of paired data were inspected for evidence of such artifacts. Excluding two samples collected on July 17 in heavily polluted coastal air, data for the UVA/AQG dichotomous sampler on the aircraft show a consistent pattern (12 of 12 observations) of unneutralized acidity (estimated as $[nss\ SO_4^{2-}] + [NO_3^-] - [NH_4^+]$ on an equivalent basis) in the fine aerosol fraction of BL air. Relative to HCl measured with fine filter packs, concentrations of HCl from concurrent bulk filter packs were systematically higher (11 of 12 cases) by an average factor of 2.3. These observations are consistent with the hypothesis that acidic fine aerosol reacted with sea-salt aerosol on bulk prefilters to produce artifact HCl and Cl^- deficits.

Six data pairs for the AOML hivol and URI cascade impactor, which were generated during overlapping but not entirely concurrent sampling periods, were also inspected for evidence of such artifacts. Cl^- deficits measured with the AOML hivol were higher relative to those for the impactors in four of six cases by an average factor for all data pairs of 2.1. Unneutralized acidity estimated for fine fraction aerosol (stages 5 and 6 of the impactor) could account for approximately 50% of the observed average difference. This suggests that particle-to-particle reactions, though potentially important, did not generate all of the artifact Cl^- deficit inferred from differences between the paired observations.

The presence of alkaline material such as sea-salt aerosol on bulk filters could scavenge HNO_3 [e.g., Savoie et al., 1989] and SO_2 [e.g., Coutant, 1977] from the airstream, resulting in the production of artifact HCl and Cl^- deficits via reactions (1) and (2). Paired data from the UVA/AQG dichotomous sampler on the aircraft reveal significantly higher (7% on average) concentrations of SO_2 downstream of the fine aerosol prefilter relative to the bulk aerosol prefilter [Bardwell et al., 1990], suggesting that SO_2 may have been scavenged by sea-salt on the bulk prefilter. If the scavenged SO_2 reacted to produce HCl, the average positive bias in HCl would be less than 5%. Because HNO_3 was apparently lost on the wall of the cyclone [Bardwell et al., 1990], paired measurements of HNO_3 could not be assessed similarly for evidence of artifacts.

Data from the AOML hivol and the URI cascade impactor were also inspected for evidence of gas-to-particle reactions on bulk aerosol filters. Concentrations of nss SO_4^{2-} and NO_3^- were summed for all stages of each impactor sample and compared with the corresponding sum for each hivol. Sums for hivol samples were greater that those for cascades in five of six cases by an average factor for all data of 1.3. Higher Cl^- deficits were observed in four of the five cases where hivol sums exceeded those for cascades. These relationships suggest that alkaline-reactive S and N gases may have been scavenged by sea-salt aerosol on the bulk filter, leading to artifact Cl^- deficits.

The above assessment indicates that particle-to-particle and gas-to-particle reactions on bulk filters may be important sources of bias in measurements of HCl and Cl^- deficits. A more detailed evaluation is available upon request from the authors.

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