SHORT CONTRIBUTION

Gaseous HCl at a remote tropical continental site

By EUGENIO SANHUEZA* and ANGEL GARABOTO, *IVIC, Atmospheric Chemistry Laboratory, Apartado 21827, Caracas 1020A, Venezuela*

ABSTRACT

Hydrochloric acid was measured in Parupa (5°41′N; 61°33′W), Canaima National Park, a pristine region located in the southern part of Venezuela, during January and September 2000. During both periods the HCl concentration was quite variable, with relatively higher levels during September and an overall median value of 37 pptv. An analysis of possible sources suggests that the photo-oxidation of chlorocarbons should be a significant source of HCl at the Parupa site.

1. Introduction

Gaseous hydrochloric acid (HCl) is a ubiquitous compound in the atmosphere. Sources include degassing of sea salt, fossil fuel combustion, waste incineration, volcanoes (e.g., Keene et al., 1999) and photo-oxidation of chlorocarbons (Sanhueza, 2000, 2001). Measurements of gaseous HCl have been reviewed by Graedel and Keene (1995). As far as we know, until now, no measurements have been reported for a tropical continental site. In this communication, we report daytime HCl levels measured at a remote continental site in Venezuela. Simultaneous CO measurements, to check for combustion sources, are also given.

2. Field measurements

Measurements were made at the Parupa Scientific Station (5°41′N; 61°33′W; ~1200 m a.s.l.), La Gran Sabana, Canaima National Park, which is located in the southeastern part of Venezuela, in the physiographic

*Corresponding author.
e-mail: esanhuez@quimica.ivic.ve

region known as the Guayana Highlands. The regional geology is dominated by the Guayana Shield and, hydrologically, it is part of the eastern Guayana watershed draining towards the Caroní River. Characteristically, flat topped mountains, locally known as Tepuys, emerge sharply from the rolling hill terrain showing highly differentiated vegetation at their summit. The western part of the park is mostly covered by tropical moist forests, while the eastern part is a mosaic of forests, shrubs and grass savannah. The Parupa Station is located in the eastern part and is mainly surrounded by grass savannahs. Annual mean temperature in Parupa is 22.5 °C and the annual precipitation 1515 mm.

Gas-phase HCl was sampled, 2 m above the surface, using the aqueous scrubber technique (Cofer et al., 1985); other details of our sampling procedure are given in Sanhueza et al. (1996). The sampled air volume was determined with a dry gas meter, and the sampling period ranged from 2 to 4 h at a flux rate of 10–12 L min^{-1}. The sample solutions were analyzed immediately after collection by ion-exchange chromatography, using a Dionex (model QIC) chromatograph equipped with a HPIC-AS4 separator column, an anion micromembrane suppressor column, and a conductivity detector. Carbonate eluent (2.8 mM

HCO_3^-/2.5 mM CO_3^{2-}) and sulfuric acid regenerant (5 mM) were used for the analysis of inorganic anions. The detection limit, for 2.5 m^3 sampled air, was 8 pptv. Carbon monoxide air concentrations were determined using a CO analyzer (Trace Analytical, model RG A3), which was equipped with a reduction-gas-detector and a molecular sieve 5A column for CO separation. Other details are given elsewhere (Sanhueza et al., 1999).

3. Results and discussion

The daytime levels of HCl and CO, measured during the January and September field campaigns, are given in Table 1. The low levels of CO indicate that, during the measurement periods, the site was not affected by emissions from combustion sources. During both measurement periods the HCl concentration was quite variable, with relatively higher concentra-

Table 1. *Concentrations of HCl and CO at the Parupa site (5°41′N; 61°33′W) during January and September 2000 campaigns*

Date	Time period	HCl (pptv)	CO (ppbv)
24/01/00	13:12–17:36	44	48
26/01/00	10:33–14:30	19	46
27/01/00	10:24–14:40	26	46
27/01/00	15:40–19:15	BDL	47
29/01/00	10:40–15:15	13	46
29/01/00	15:50–20:10	30	51
30/01/00	10:15–14:25	80	51
30/01/00	14:55–19:15	32	55
31/01/00	10:00–14:20	BDL[a]	MD[b]
31/01/00	14:55–19:10	10	48
13/09/00	9:00–12:00	41	40
13/09/00	13:45–16:45	29	41
15/09/00	9:10–12:00	84	50
15/09/00	13:30–16:30	59	49
15/09/00	17:25–20:20	119	55
16/09/00	9:10–11:50	75	52
16/09/00	14:00–17:00	52	51
16/09/00	17:45–20:45	13	MD
17/09/00	8:15–11:15	83	54
17/09/00	11:55–14:55	88	50
17/09/00	15:35–18:00	66	50
18/09/00	9:00–11:30	31	46
18/09/00	12:40–15:00	46	38
18/09/00	15:40–19:00	20	44
19/09/00	8:25–11:25	26	48
19/09/00	12:00–15:00	33	44
19/09/00	15:35–18:00	141	68

[a]BDL, Below detection limit. [b]MD, Missing data.

tions during September and an overall median value of 37 pptv (overall average 54 ± 37 pptv). The HCl levels at the Parupa site, are lower than the values found in remote oceanic regions (100–300 pptv) and it is in the lower part of the large range (10–2000 pptv) measured at rural continental sites (Graedel and Keene, 1995).

The amount of HCl produced from sea-salt acid displacement is very uncertain: Graedel and Keene (1995) estimated a global flux of 50 ± 20 Tg Cl yr^{-1}, whereas, more recently, Erickson et al. (1999) indicated that this source only produces ∼7.6 Tg Cl yr^{-1}. The production of HCl from acid-displacement involves inorganic acidic gases, mainly emitted by anthropogenic sources (Erickson et al., 1999). Accordingly, Ayers et al. (1999) found a very small Cl loss from marine aerosols in clean air. Therefore, considering the distance to the ocean (over 350 km) and the lack of significant anthropogenic sources of inorganic acid precursors in the region (suggested by very low levels of CO and aromatic hydrocarbons; Holzinger et al., 2001), it is unlikely that the HCl produced from sea-salt acid displacement makes a significant contribution to the HCl observed at the Parupa site. Also, since the region is not affected by volcanic emissions, and since during the measurement campaigns the site was not affected by biomass burning, it is most likely that the observed HCl, is produced during the photo-oxidation of chlorocarbon compounds (Sanhueza, 2000, 2001).

Recently, Sanhueza (2001) proposed that the oxidation of chlorocarbons is a significant global source of HCl (4.2 Tg Cl yr^{-1}). The regional production of HCl, in the tropical atmosphere, is presented in Table 2. The reaction mechanisms, initiated by the OH radical, to produce HCl were discussed previously (Sanhueza, 2000, 2001). According with the results (Table 2), in the tropical troposphere, a production of 1.7–3.4 ppbv yr^{-1} of gaseous HCl is expected from the oxidation of chlorocarbons.

Tropical savannah surface daytime measurements are quite representative of boundary layer conditions (e.g., Sanhueza et al., 2000); however, since the lifetime of HCl in the lower troposphere is 1–2 d (Graedel and Keene, 1995), it is expected that higher levels of HCl are produced in the free troposphere. Taking this into consideration, and assuming that the degradation of chlorocarbons is the primary source of HCl, a rough calculation indicates that an atmospheric concentration of ∼40 ppbv (as found in Parupa), would be consistent with a HCl tropospheric lifetime of 4–8 d. This longer lifetime, compared to that of the boundary

Table 2. *Production of HCl from the phochemical oxidation of clorocarbons (RCl)*[a]

RCl	Tropical [RCl] (pptv)	K_{OH} (263 K)[b] ($\times 10^{14}$ cm^3 molecule^{-1} s^{-1})	-dRCl/dt (ppbv yr^{-1})	Production of gaseous HCl (ppbv yr^{-1})
CH_3Cl	620[c]	2.63	0.77–1.54	0.77–1.54
CH_2Cl_2	NH: 40–50[d]	8.8	0.19–0.37	0.37–0.75
	SH: 15–20			
$CHCl_3$	NH: 17.3[e]	6.4	0.05–0.11	0.05–0.11
	SH: 9.7			
CH_3CCl_3	160[f]	0.56	0.04–0.08	0.04–0.08
CH_2ClCH_2Cl	12[g]	14[g]	0.08–0.16	0.08–0.16
$CHClCCl_2$	NH: 2[h]	284	0.27–0.54	0.27–0.54
	SH: 0.5			
CCl_2CCl_2	NH: 7[i]	9.8	0.03–0.06	?
	SH: 2.2			
CHF_2Cl	117[d]	0.23	0.013–0.025	0.013–0.025
			Total	1.7–3.4

NH, Northern Hemisphere; SH, Southern Hemisphere. [a]Adapted from Sanhueza (2000). The OH concentration used ranged from 1.5×10^6 to 3×10^6 molecules cm^{-3} (Crutzen et al., 1994; Crutzen, 1996). [b]Atkinson (1986). [c]Khalil and Rasmussen (1999a). [d]Kurylo and Rodriguez (1999). [e]Khalil and Rasmussen (1999b). [f]Sanhueza et al. (1995). [g]Class and Ballschmiter (1987). [h]Kindler et al. (1995). [i]Wiedmann et al. (1994).

layer, is quite reasonable if we consider that higher HCl concentrations should be produced in the upper troposphere.

In conclusion, the measurements made in Parupa (clean tropical atmosphere) support the proposal that the oxidation of chlorocarbons should be a significant source of HCl in the remote troposphere, and that this acid may significantly contribute to the acidity of background rains (Sanhueza, 2001).

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