

An Upper Limit on the HCl Near-Surface Mixing Ratio over the Atlantic Measured Using TDLAS

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Abstract. A study of the gas phase mixing ratio of hydrochloric acid was made during the 1988 *Polarstern* expedition using tunable diode laser absorption spectroscopy (TDLAS). The measurements were made 22 m above sea level at 28° N, 30° W. The signal-to-noise ratio was unity for <50 pptv HCl, but because of wall effects in the sampling system, only an upper limit for the HCl mixing ratio of <250 pptv can be stated.

Key words: Hydrochloric acid, chlorine cycle, maritime troposphere, TDLAS, boundary layer.

1. Introduction

There is general agreement that gas phase HCl may be released from the sea-salt aerosol following acidification by strong acids such as H₂SO₄ and HNO₃ (Cicerone, 1981 and references therein), as well as by methanesulphonic acid (Brimblecombe and Clegg, 1988).

Attention has recently been drawn to the potential importance of sea-salt-related sources of chlorine in the troposphere by Singh and Kasting (1988), who noted that Cl atoms, released after reaction of OH with HCl, are very much more reactive towards many nonmethane hydrocarbons (NMHC) than are OH radicals themselves. Using a detailed one-dimensional model, Singh and Kasting (1988), showed that if the mean mixing ratio of HCl in the marine boundary layer is 0.5–2 ppbv, then the fractional amount of NMHC oxidized by Cl atoms relative to the total amount oxidized by Cl and OH in the troposphere, lies between 20 and 40%, which would indicate that Cl plays a very significant role in the global atmospheric chemistry of NMHC.

However, it is uncertain what a reasonable average value for the boundary layer HCl mixing ratio might be. Several measurements of 'Gaseous Inorganic Chlorine', (GIC), as collected on LiOH or K₂CO₃ filters, are summarized by Cicerone (1981) and Brimblecombe and Clegg (1988), and suggest the range used in the model by Singh and Kasting. However, the majority of these data were obtained at either continental or coastal locations, and even if the measured quantities were correctly

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interpreted as entirely gas phase HCl, the results may not be typical of the remote oceanic boundary layer. A recent study by Keene *et al.* (1990), found HCl mixing ratios mostly below 1.0 ppbv near the U.S. Atlantic coast which decreased with altitude and distance from the continent. These authors, who used a dichotomous filter pack consisting of a quartz front filter for aerosols and a K_2CO_3 impregnated rayon back filter for gas phase species, warn that particle-to-particle and gas-to-particle reactions on the bulk aerosol pre-filter may cause a large (factor of two) positive bias in the estimate of gas phase HCl using this technique.

Measurements by an HCl-specific derivatization GC technique (Vierkorn-Rudolph *et al.*, 1984a, b; Matusca *et al.*, 1984), yielded values of 50 to 100 pptv for Atlantic airmasses uninfluenced by continents, while indicating higher values in air masses that had recently travelled inland (Vierkorn-Rudolph *et al.*, 1984a, b).

We know of two ground-based FTIR studies of tropospheric HCl, Marché *et al.* (1980), report tropospheric column amounts of $0.15\text{--}0.70 \times 10^{15}$ molec cm^{-2} over Rheims, (49° N, 4° E) and mixing ratios in the lowest layers of 1–100 pptv. Farmer *et al.* (1976) observed higher tropospheric column amounts of $7\text{--}11 \times 10^{15}$ molec cm^{-2} at several sites in the west of the U.S.A. These authors did not report a surface-level mixing ratio but normalized their measured column abundance to the surface values of ~ 1 ppbv (GIC) obtained by Junge (1957) at Hawaii, in order to deduce a scale height for HCl. This procedure was apparently misinterpreted as support for ground-level HCl mixing ratios near 1 ppbv by Singh and Kasting (1988).

Thus, there appears to be considerable doubt as to whether the maritime boundary-layer mixing ratios for HCl lie in the ppbv range as suggested by one group of measurements, or considerably lower as suggested by a second group. To obtain further information on HCl in remote oceanic air, we made exploratory measurements using our TDLAS spectrometer during the *Polarstern* cruise.

2. Experimental

Measurements were made with high specificity by monitoring the absorption on the $H^{35}Cl$ R(1) line at 2925.90 cm^{-1} in our 1.5 m base path, Teflon-lined White cell, which was set for a total optical path of 213 m. An appropriate Pb-salt laser diode was made available to us by the Fraunhofer-Institut für Physikalische Meßtechnik, Freiburg, F.R.G. The total pressure in the White cell was 50 mbar and ambient air could be pumped through the cell (volume 28 l) at a rate of up to ~ 10 slm, resulting in a gas residence time of ~ 1.5 s.

The spectrometer as a whole (including the all-Teflon inlet system) was calibrated (Harris *et al.*, 1992) by the addition of HCl from a permeation device consisted of a thermostatted glass reservoir of 37% HCl solution in which a length of 0.125 inch outside diameter Teflon tube was immersed. HCl permeated through the walls of the tube and was carried away by a flow of 50 sccm of dry N_2 . The mass permeation rate of the device was determined by timed acid-base titration against a NaOH solution in an impinger to be $36 \pm 4\text{ ng min}^{-1}$ at $40 \pm 0.5^\circ\text{C}$.

Addition of the HCl calibration gas to a flow of 9.0 slm of dry nitrogen passing through the White cell resulted in a calibration mixture of 2.46 ± 0.3 ppbv. The instrumental precision towards HCl for 60 s signal-averaging times was determined from the standard deviation of the calibration signal after a stabilization period of about one hour and from the reproducibility of previously obtained background spectra. The precision deduced from the data in Figure 1 is $< \sim 50$ pptv HCl.

HCl is a polar molecule and interaction of the gas phase species with the surfaces of the inlet and White cell is to be expected. In our system, we observed long-lasting memory effects which limited our ability to measure very low HCl mixing ratios (see below). Other investigators, using TDLAS for HCl measurement in White cells, have reported similar problems. Brassington (1989) observed that 90% of a 20 ppbv calibration spike disappeared a few seconds after removing the HCl source, but that the remaining 10% decayed more slowly, approaching his instrument noise level of 0.4 ppbv peak-to-peak with a time constant of ~ 60 s. Our measurements suggest a third part to the fall-off behaviour at levels near and below

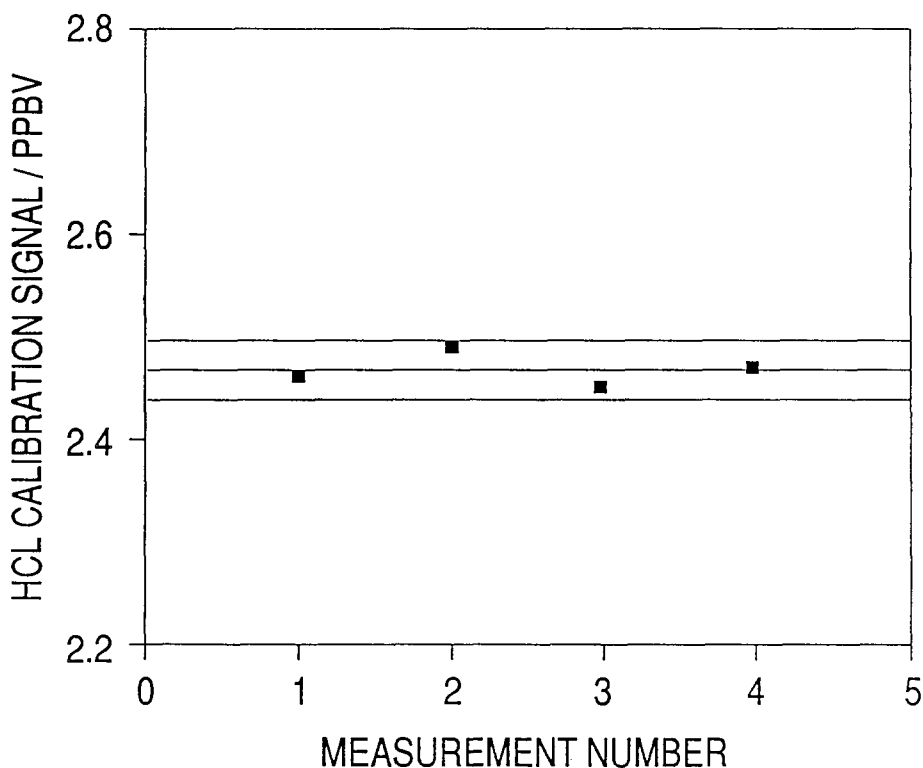


Fig. 1. Calibration signal reproducibility for a calculated HCl mixing ratio of 2.46 ppbv. The effective measurement bandwidth for each point was ~ 0.1 Hz. The horizontal lines show the mean and $\pm 2\sigma$ values for the data.

Brassington's detection limits, which is characterized by a much longer time constant. Freid *et al.* (1983) reported similar long-term memory effects.

We declined to employ alternative calibration methods, for example using a short cell containing ppmv HCl mixtures external to the White cell, since we believe that it is important, most especially in cases where interactions with the inlet system occur, to calibrate the complete system. Calibration methods which yield information only on the mixing ratio of the target gas in the White cell, rather than in the air being sampled, are to be avoided.

3. Results and Discussion

The measurements aboard *Polarstern* were carried out on 24 September 1988 at position 28° N, 30° W, under cloudless conditions, a wind speed of 5 m s⁻¹, relative humidity 65% and air temperature 23° C, the latter parameters being measured by the ship's sensors ~6 m above our sample inlet.

Because of the memory effects discussed above, only an upper limit for the HCl mixing ratio of <250 pptv could be determined from the TDLAS data. The observed HCl signal decreased to half its initial value of 2.5 ppbv within 5 min of the removal of the calibration spike, (Figure 2), but thereafter dropped much more slowly, reaching an apparently stable level of ~250 pptv only after three hours had elapsed. This constant signal was observed for a further two hours (between 13:00 and 15:00 local time), thus for considerably longer than the previously observed rise time for the calibration signal, and by inference longer than the rise time for an ambient signal. The observed signal may then represent the ambient HCl mixing ratio at the site. However, tests in which the air flow was replaced by dry N₂ for several minutes suggested that much of the remaining signal may still have been due to surface off-gassing following the earlier exposure to calibration gas, rather than being due to ambient HCl. We therefore believe that the actual HCl mixing ratio in air was less than indicated by the signal intensity and thus quote only an upper limit.

While our measurements were carried out relatively near to the surface of the ocean, and a concentration gradient in the lowest part of the atmosphere is possible, the data indicate that the HCl mixing ratio at our site was below the range adopted by Singh and Kasting (1988) for their modelling study. Gas phase HNO₃ and aerosol NO₃⁻, measured by other investigators on *Polarstern*, (Papenbrock and Stuhl, 1990; Müller *et al.*, 1990), suggest values of ~100 pptv and ~5 × 10⁻⁷ g m⁻³, respectively, during our measurement period. Presumably the production of HCl from sea-salt is limited by the availability of strong acids in the remote maritime environment. HNO₃ mixing ratios in excess of 100 pptv were only occasionally observed during the *Polarstern* cruise (Papenbrock and Stuhl, 1990).

Based on the study by Singh and Kasting, we estimate that if the upper limit of 0.25 ppbv HCl estimated here were to be typical, then less than 5% of NMHC near the surface is oxidized through chlorine chemistry initiated by OH attack on HCl,

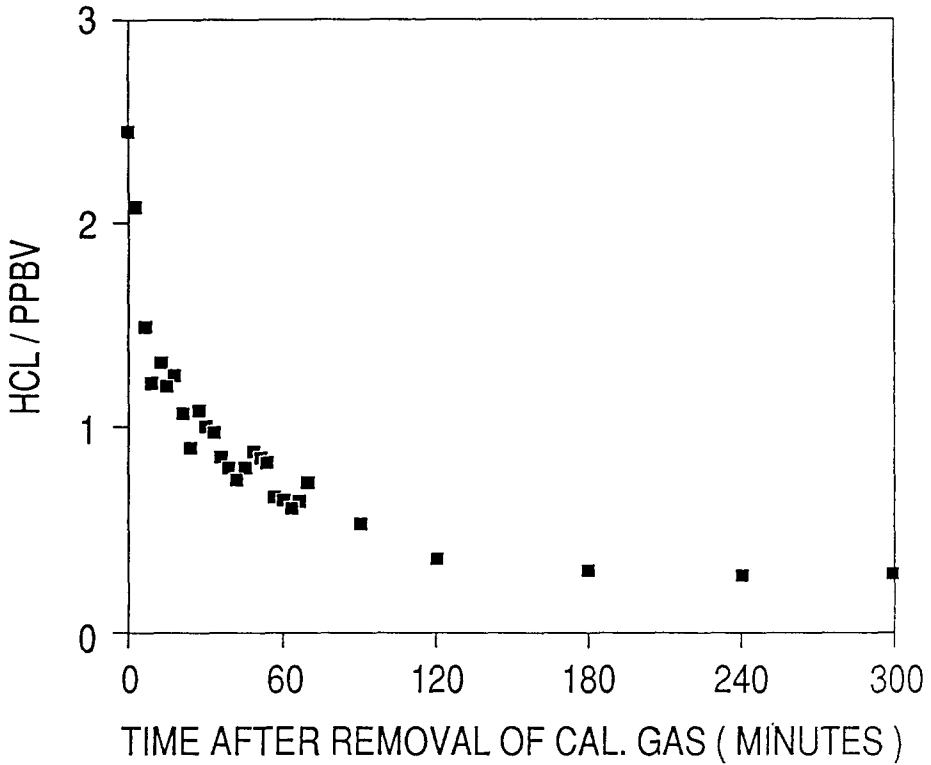


Fig. 2. Time dependence of the observed HCl signal intensity after replacement of the 2.46 ppbv HCl in N_2 calibration flow by ambient air.

however the potential importance of Cl chemistry, perhaps especially in coastal regions, is such that further effort is warranted to overcome the technical problems associated with direct measurement of HCl encountered in this work.

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