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INVERSE PROBLEMS  
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## Consideration of High Surface Concentrations of Hydrochloric Acid Vapors in Ground-Based Spectroscopic Measurements

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**Abstract**—Spectral measurements show that solar radiation can contain information on extremely high surface concentrations of hydrochloric acid vapors, which leads to the impossibility of estimation of their total content using the background a priori information. An alternative specification of a priori information is suggested, which allows an increase in the number of retrieved values of hydrochloric acid vapor by 10%. The existence of high surface concentrations of the gas is confirmed by the spectral data processing results. A good agreement between estimates of the stratospheric content of hydrochloric acid vapors retrieved from ground-based measurements using the proposed a priori information and independent satellite data is shown: mean differences between data received by the two methods are 4.4%, standard deviation of the differences is 5.7%, and the correlation coefficient is 0.85.

*Keywords:* ground-based spectroscopic measurements, gas total content, hydrochloric acid vapors in the atmosphere, near-surface pollution of the atmosphere

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### INTRODUCTION

The ground-based technique for measuring the total content (TC) of atmospheric trace gases on the basis of high-resolution spectral measurements of solar IR radiation has been successfully used for several decades (see, e.g., [1]). Among many atmospheric trace gases, gases connected with photochemical processes with the participation of ozone are of special interest, such as hydrochloric acid (HCl) vapors, which are a stratospheric reservoir of chlorine. In view of the analysis of photochemical processes in the ozoneosphere, the primary focus is on the stratospheric content (SC) of ozone.

HCl is a common material on the Earth's surface; it participates in vital processes of almost all animals and men, is used in the chemical industry in vinyl chloride production and in electrolytic processes during metal treatment, etc. [2]. Therefore, the presence of this gas in the boundary air layer in noticeable concentrations is probable. The width of spectral absorption lines in the IR region is much larger under the surface pressure than in the stratosphere, which allows discrimination of contributions of the two altitude ranges in the absorption. Nevertheless, an approach usually used in the international Network for the Detection of Atmospheric Composition Change (NDACC) supposes use of a background HCl vapor concentration profile as a priori information; this concentration is characterized by low values in the boundary air layer and a constant a priori relative variability of ~20–30% (hereinafter, traditional

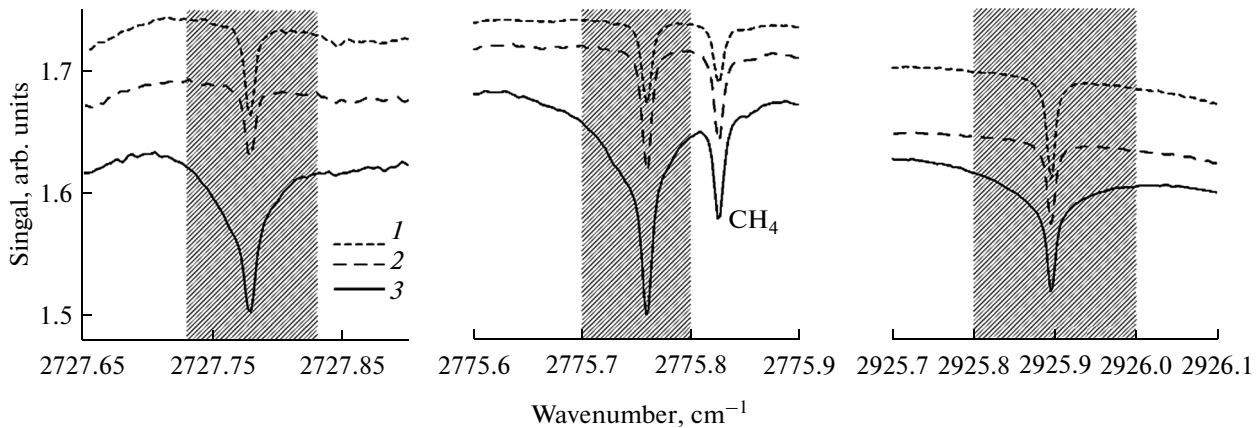
a priori information is designated as TAI). Such a priori information automatically limits mixture ratios calculated for the boundary air layer, which either makes impossible solution of the inverse problem or results in overestimated values.

In this work, we suggest an approach to the solution of the inverse problem of retrieval of HCl SC under assumption of significant variations in the HCl concentration in the boundary air layer. The corresponding a priori information is called new and further designated as NAI.

### 1. MEASUREMENTS OF TC HCL

Ground-based measurements of IR spectra of direct solar radiation on the basis of a high-resolution Fourier spectrometer IFS-125HR have been carried out by researchers of St. Petersburg University (Department of Atmospheric Physics, Physics Faculty) 28 km to the west of the center of St. Petersburg (59°88' N, 29°82' E). These measurements allow the TC of some important climatically active gases to be found [4].

Total HCl column measurement results are described in [5], including measurement technique and data interpretation, measurement errors, comparison with measurements at the nearest NDACC stations and satellite measurements, and the analysis of seasonal variations in the total HCl column. In the study of the total HCl column, from 1 to 15 spectra are measured per day, usually 5–6. The spectra measured



**Fig. 1.** Spectra recorded at 11:34 (1), 13:26 (2), and 16:50 (3) on April 26, 2010 in ranges that include microwindows (shaded) used for HCl TC calculations. The high-intensive lines in the middle of each range belong to HCl.

with the use of the Norton–Beer medium apodization function have a spectral resolution of  $0.0083 \text{ cm}^{-1}$ . The signal-to-noise ratio found from the hash of zero signal varies in the 300–1600 limits; the typical value is 1000. SFIT2 software, used at NDACC stations, was used as a technique for interpreting the measurements. The spectral ranges  $2727.73\text{--}2727.83$ ;  $2775.70\text{--}2775.80$ , and  $2925.80\text{--}2926.00 \text{ cm}^{-1}$ , recommended for the total HCl column measurements in NDACC, were used. In addition to HCl, methane, water vapor, ozone, nitrogen oxide and dioxide affect the absorption in these ranges. Quantitative parameters of the molecular absorption for all atmospheric gases were taken from HITRAN 2008 database [6].

To calculate the TC of a gas in SFIT2, we have chosen the mode in which the profile of gas mixing ratio is retrieved and the total content is calculated via its integration. The profile retrieval is an intermediate step, and the information content of the ground-based measurements with respect to HCl profile is low (2–4 independent parameters); therefore, the software uses a priori information in the form of average profiles and covariance matrices for regularization of solution of the incorrect inverse problem. The constant average profile from the WACCM model [7] version 5 for St. Petersburg serves an a priori profile. An a priori exponential covariance matrix was also used in the standard approach at 20-% relative variability of the HCl concentration at all levels.

Since the information content of the problem is low, the spectra cannot contain information about small-scale details of the profile, and the correlation radius of the matrix was chosen as 15 km to suppress high-frequency noise during the calculations. When solving the inverse problem, additional profiles of noise gases are refined; WACCM data on the monthly average profiles for each month and year were used as a priori information about these gases. In addition, the air temperature profile was used, and the water vapor

mixing ratio profile (as an initial approximation) from Voyeykovo (26063 ULLI) radio sounding measurement data supplemented for the upper atmosphere and, if necessary, for other altitudes with AQUA satellite level 3 data (AIRS and AMSU-A instruments) [8] for each measurement day. The inverse problem was solved in the iterative mode (mean number of iterations was 8). The relative standard difference between the calculated (after the solution of the inverse problem) and experimental solar spectra was  $\sim 0.6\%$ . The total systematic and random TC errors were 3.8 and 4.5% [5]. The daily variations in the HCl TC were less than 1% (estimate of the random component of the errors) under optically stable measurement conditions and stable instrument operation.

According to the experience of interpretation of ground-based measurements, some spectra measured did not allow convergence of the iteration process of inverse problem solution during calculation of HCl TC; this was caused by uncontrollable errors in the initial data in most cases. However, the nonconvergence was sometimes caused by abnormal CHI concentrations in the air in Peterhof and the related inadequacy of the a priori information used. Figure 1 exemplifies spectra measured in the spectral ranges used in HCl TC calculations at different time on April 26, 2010.

As seen from Fig. 1, all HCl absorption lines measured at 16:50 show much stronger solar radiation absorption and much wider profiles as compared to lines measured at other times. A similar pattern was observed for HCl lines out of the ranges shown. It is important that lines of other gases (e.g., methane line near  $2775.83 \text{ cm}^{-1}$ , Fig. 1b) were almost invariant at the same time, which points to the absence of general spectral distortions and the specificity of the effect observed just for HCl.

**Table 1.** Comparison (statistical parameters of relative differences of individual measurements) for two a priori statistics, %

| Parameter          | TC  | SC <sub>200</sub> | SC <sub>100</sub> |
|--------------------|-----|-------------------|-------------------|
| Mean difference    | 8.1 | -0.8              | 0.7               |
| Standard deviation | 7.8 | 1.1               | 0.6               |

## 2. INTERPRETATION TECHNIQUE WITH USE OF NAI

As seen from Fig. 1, significant HCl concentrations can be observed in the tropospheric air layer in Peterhof. This can be considered during the interpretation of measurements with the use of new covariance matrices, which admit higher variations in the HCl concentration in the surface air layer. In this case, we keep the a priori profile of HCl concentration corresponding to the background atmosphere and use an inhomogeneous covariance matrix  $\mathbf{D}$  composed of two independent blocks. Above the boundary specified, we use the exponential matrix (with a fixed correlation radius and constant relative variability) from [5], and below, we significantly increase the variability and decrease the correlation radius. A zero correlation between gas concentrations above and below the boundary is assumed, i.e., the surface and free-air gas concentrations are unrelated. Thus, elements of the model a priori matrix are calculated by the equation

$$d_{i,j} = \begin{cases} \sigma_s^2 \exp\left(-\frac{|z_i - z_j|}{r_s}\right), & \text{if } z_i > z_t, z_j > z_t, \\ 0, & \text{if } z_i < z_t, z_j > z_t \\ & \text{or } z_i > z_t, z_j < z_t, \\ \sigma_t^2 \exp\left(-\frac{|z_i - z_j|}{r_t}\right), & \text{if } z_i < z_t, z_j < z_t. \end{cases} \quad (1)$$

Here  $d_{i,j}$  is the element of the a priori covariance matrix  $\mathbf{D}$ , rel. units;  $i$  and  $j$  are the indices of levels in the atmosphere;  $z_i$  and  $z_j$  are the altitudes of the corresponding levels;  $\sigma_t$ ,  $\sigma_s$ ,  $r_t$ ,  $r_s$  are the relative variabilities and correlation radii for a distinguished boundary layer and other atmosphere;  $z_t$  is the altitude of the upper boundary of the boundary layer selected.

Different altitudes were used for the two-block a priori matrix and the surface layer (from 1 to 8 km) and different values of a priori variability (from 200 to 20000%). This NAI was used for the calculation of the total HCl column and, conventionally, its stratospheric content, i.e., above 100 or 200 mbar. Below, along with the HCl TC, we consider its stratospheric content, i.e., the total HCl column above the level determined by a terminal pressure of 100 or 200 mbar (SC<sub>100</sub>, SC<sub>200</sub>).

## 3. NUMERICAL STUDY RESULTS

Let us first analyze how the use of different NAI affects the retrieval of HCl concentration on April 26, 2010. Six spectra were measured that day, which included spectral regions required for HCl retrieval. First four measurements do not differ from others, but measurements at 16:40 and 17:04 show high absorption in HCl lines under high pressures (see Fig. 1) and non-convergence of the iteration process of the inverse problem solution. Solution of the inverse problem for these two measurements with different variants of NAI allowed a conclusion that the solution of the inverse problem converges, and stratospheric HCl concentrations measured that day almost coincide under a priori variability in the bottom layer of 20000%. SC<sub>100</sub> varied by less than 2% during the day, and estimates of the HCl concentration below the 100-mbar level were extremely high: 20–35 cm<sup>-2</sup> at 15:50 and 15–20 × 10<sup>15</sup> cm<sup>-2</sup> at 17:04, depending on a NAI variant. One can assume that a “cloud” with a high HCl concentration passed at the instants of measurements of these two spectra.

Control of HCl SC is an important problem in ground-based measurements. In view of this, let us analyze the results of HCl SC retrieval above 100 or 200 mbar (SC<sub>100</sub> and SC<sub>200</sub>) in the cases of using different a priori information for the surface air layer or the troposphere. To control the SC retrieval quality, we use satellite MLS sounding data of HCl SC [9]. The comparison with satellite data allows optimal NAI parameters to be chosen, i.e., a surface air thickness of 2 km with relative a priori variability of 2000% inside it. After the optimal parameters of NAI were chosen, the entire measurement array for five years (2009–2014) was processed.

As a result, the inverse problem solution was found (convergent iterative process) in 287 cases, in which TAI gives no solution. Table 1 shows how the gas content retrieval results changed in different air layers when transferring from TAI to NAI.

It is seen that the mean difference and its standard deviation exceed insignificantly 1% for SC<sub>100</sub> and SC<sub>200</sub>. They are much lower than the above estimates of the HCl TC errors; they can be obviously considered negligible, in contrast to variations in HCl TC. When the standard deviation of the difference is 7.8%, the increase in the average HCl TC by 8.1% is apparently caused just by assumed high surface concentrations of the gas.

Let us also note that daily variations in SC<sub>100</sub> decrease from 4.2 to 3.9% when transferring from TAI to NAI, which witnesses some stabilization of the values and a decrease in the random measurement error.

**Table 2.** Comparison of ground-based and satellite measurements of HCl TC and stratospheric contents  $SC_{100}$  and  $SC_{200}$  when using TAI and NAI

| Statistical parameter   | TC   |      | $SC_{200}$ |      | $SC_{100}$ |      |
|-------------------------|------|------|------------|------|------------|------|
|                         | TAI  | NAI  | TAI        | NAI  | TAI        | NAI  |
| Mean difference, %      | 6.0  | -2.7 | 7.4        | 8.3  | 5.1        | 4.4  |
| Standard deviation, %   | 9.6  | 12.9 | 8.7        | 8.6  | 5.7        | 5.7  |
| Correlation coefficient | 0.75 | 0.63 | 0.78       | 0.78 | 0.85       | 0.85 |

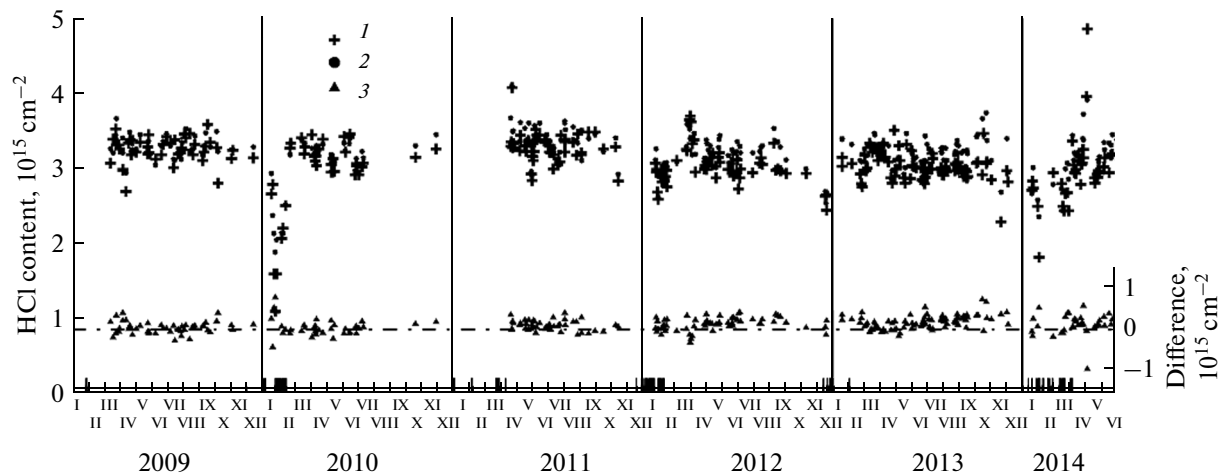
#### 4. ANALYSIS OF INTERPRETATION RESULTS AND COMPARISON WITH INDEPENDENT MEASUREMENT RESULTS

We have compared the values calculated with AURA MLS measurement data [9]. Let us note that the satellite data are represented by vertical profiles usually known at a level of 150 mbar and higher. That is why we could directly compare  $SC_{100}$  profiles calculated on the basis of satellite data. Below this level, the HCl TC and  $SC_{200}$  profiles were supplemented by monthly average climatic norms. Ground-based measured HCl SC and MLS data are compared in Table 2 for the cases of using different a priori information.

As seen from Table 2, though the mean difference between these two types of TC measurements decreased in absolute values when using NAI, the standard deviation of the difference increased from 9.6 to 12.9%, and the correlation coefficient (CC) decreased. This is apparently connected with the total absence of satellite data in the boundary layer and the use of climatic norms inside them to supplement the profiles, while actual TC values are used in the ground-based measurements. The situation differs for the stratospheric content. The mean difference increases insignificantly (less by 1%) when

transferring from TAI to NAI (apparently, again due to supplement of the profiles with the climatic norms), but the standard deviation of the difference and CC do not change. The situation for  $SC_{100}$  is similar, except for the 0.7-% decrease in the mean difference when using NAI. Though the differences are small, they witness that the use of NAI does not worsen the agreement between ground-based SC measurements and satellite measurements in the cases where the iterative process converges for both types of a priori information, which allows estimation of the TC.

The ground-based and satellite  $SC_{100}$  measurements are compared in Fig. 2. The daily average measurement results are shown for one day. The triangles show differences (right scale) between ground-based and satellite measurements. A very good agreement between the two types of measurements is evident even for the periods of sharp variations in the HCl SC during measurements in a polar vortex. The presence of the polar vortex is marked on the abscissa according to the criterion [10], i.e., the potential vorticity (we consider daily average values from the website apps.ecmwf.int) higher a threshold of  $4.2 \times 10^{-5} \text{ K m}^2/(\text{kg s})$  on the 475 K isentropic level.



**Fig. 2.** Comparison between ground-based and satellite measurements of HCl SC: ground-based measurements (1), satellite data (2), and the difference (3). The marks on the abscissa show propagation of a polar vortex in the region of ground-based measurements.

## CONCLUSIONS

1. Atmospheric HCl concentrations measured at St. Petersburg State University in 2009–2014 with the use of high-resolution spectroscopy of solar IR radiation show high values in the surface air layer in some cases. A priori information used in algorithm for interpretation of NDACC ground-based measurements does not allow solution of the inverse problem in these cases.

2. The use of new a priori information in the surface air layer with high variability (2000–20000% in the surface air layer of 1–2 km in thickness) for solution of the inverse problem allowed an increase in the number of successful retrievals of HCl concentration by more than 10%.

3. The comparison of HCl SC found with independent satellite data has shown that the use of the above a priori statistics does not increase the difference between the ground-based and satellite measurements.

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