Latitudinal variations of the vertical profiles and columnar HDO/H_2O ratio in the atmosphere over the ocean retrieved from IMG/ADEOS data

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Method of retrieving the HDO/H_2O ratio profile and its columnar value is presented. The method is based on the expansion of the profile retrieved over eigenvectors of the covariance matrix of model profiles obtained using general circulation model of the atmosphere. *A priori* information contained in the covariance matrix of the model profiles compensates partially for the lack of information in the weighting functions for HDO in the lower atmospheric layer (0–1 km) and layers above 10 km. Infrared radiance spectra observed from a satellite with high spectral resolution along nadir were used as input data for the retrievals. The method was tested using IMG/ADEOS spectra measured over the ocean under clear sky conditions. Latitudinal distributions of HDO/H_2O vertical profile and columnar value of the HDO/H_2O ratio were retrieved over Pacific Ocean for the time period from winter of 1996 to summer of 1997. Error estimation was made using closed model calculations and its value is not greater than 25‰ for vertical profile and not greater than 20‰ for columnar value of the HDO/H_2O ratio. Vertical and latitudinal distributions obtained in this paper are in a good agreement with the literature data on isotopic composition of water vapor in the atmosphere.

Introduction

Deuterium variations in the atmosphere are caused by fractionation of isotopes during vaporization and condensation.[1] Isotopic fractionation, as water vapor transits to the liquid phase and back, causes reduction of the relative content of heavy isotopes in the gas phase and the increase in their number in the liquid phase of water. Since the atmospheric part of the hydrological cycle consists in transfer of water from the ocean to the continents, then the local HDO content in the atmospheric water vapor reflects, to a certain extent, the history of precipitation for the air masses on their way from the ocean to the continents. Thus, the HDO can be a convenient tracer in the studies of the global atmospheric circulation. The studies of the relations between the isotopic composition of water vapor in air and the climatic conditions is important in cloud physics, climatology, hydrology, and paleoclimatology.[1–3]

Until recently, the main method of determining the atmospheric deuterium content has been the isotopic analysis of precipitations.[4] Since 1961, the World Meteorological Organization (WMO) and the International Atomic Energy Agency (IAEA) established a network of sampling and observing the isotopic composition of atmospheric precipitations.[5] However, most of its observation points are concentrated in Europe, so the network does not provide global data. Determination of the HDO/H_2O ratio in the atmospheric water vapor is not an easy task. For this purpose, airborne instrumentation is used for sampling that allows the studies of the vertical HDO distribution in the atmosphere.[6] Spaceborne methods of thermal atmospheric sensing allow real time global coverage measurements of the content of water vapor isotopomers with simultaneous measurement of accompanying parameters such as vertical temperature profiles, humidity, and concentration of greenhouse gases.

Quantitative deuterium content in the atmospheric layer or in the entire atmospheric column is expressed by the relation

$$\delta D = \left(\frac{R}{R_{SMOW}} - 1 \right) \cdot 1000\,‰, \qquad (1)$$

where R is the ratio between the number of deuterium atoms and the number of hydrogen atoms in a sample, and $R_{SMOW} = 1.5576 \cdot 10^{-4}$ is the average value of this ratio in the ocean water. With the account of fractionation processes that accompany water vaporization and condensation, the value of δD in the atmosphere for water vapor keeps within −1000–0‰.

Our task was the development of a technique for determining the vertical profiles of the HDO/H_2O ratio in the atmosphere based on the expansion over eigenvectors of the covariance matrix of the profiles obtained by the general circulation model of the atmosphere and testing this technique using IMG/ADEOS data. The IMG satellite sensor (Interferometric Monitor for Greenhouse Gases) is a

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Fourier spectrometer based on Michelson interferometer that operates in a 3.3–16.6 μm wavelength region with the spectral brightness noise equivalent of 0.020–0.035 μW/(cm^2 · cm^{-1} · sr).[7] Though a relatively short time of its performance (November 1996 to July 1997), the IMG data retrieved from the ADEOS satellite still are of a practical and scientific value. Atmospheric observations with the IMG/ADEOS sensor were performed along nadir.

The object of investigation was the area between 65°S – 65°N and 130–170°W in the Pacific Ocean. Among all the IMG spectra we have selected the spectra measured in this region under clear sky conditions. The technique of determining the "cloudless" spectra above water surface consisted in the analysis of the spectral dependence of the brightness temperature in the atmospheric transmission windows from 830 to 1200 cm^{-1}. The IMG daytime spectra selected in this way were additionally processed for screened clouds using data obtained with the OCTS (Ocean Color Temperature Scanner) visible-image sensor from onboard ADEOS.[8] This procedure allowed us to select the spectra corresponding to the conditions of cloudless weakly aerosoled atmosphere with a low aerosol content.[9] Overall, 1022 spectra were selected. For analysis we have chosen the spectral intervals having CO_2 absorption lines (interval 1: 680–830 cm^{-1} to reconstruct the temperature profile) and water lines of the main isotopomer and HDO (interval 2: 1192–1217 cm^{-1}, to reconstruct the δD profile) (Fig. 1).

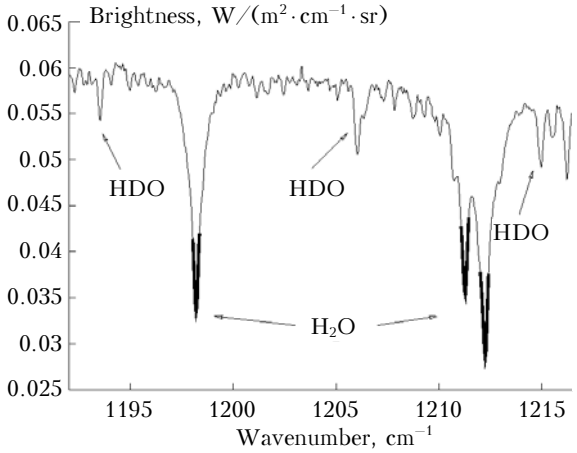

Fig. 1. The spectral interval (interval 2) for reconstruction of water vapor and δD profiles. The intervals are shown for preliminary assessment of water vapor profile.

A priori information

The *a priori* information was the data obtained with the general circulation model of the atmosphere that takes into account isotopic water separation.[10] Sets of atmospheric states covering the earth surface all over are modeled for two full years.

Spatial coverage of the Earth's surface was modeled with the step of 4° in latitude and 5° in longitude, that is, globally, simultaneous meteorology was described by a set of ~3300 points on the geographic grid. The time coverage has been done with the step of 3 h that yielded ~2800 global realizations. The atmospheric state at each point involved surface pressure (P_s), the profiles of pressure, temperature, and humidity, and the profile of isotopic ratio δD. Each profile consisted of 20 atmospheric levels (from P_s to ~ 0.1 mbar). For the vertical allocation of profiles, we used a barometric formula that takes into account the temperature profile.[11]

From the whole data set, we have selected the atmospheric states (overall, about 420 000) modeled for the period of December to July and geographically covering the specified region over the Pacific Ocean.

Technique

The atmospheric parameters were reconstructed by adjusting the calculated spectrum to the measured spectral data under variations of the corresponding atmospheric parameters. The objective function of the form

$$F = \sum_{i=1}^{M}\left[\frac{W_i^{\text{obs}}}{W_i^{\text{calc}}} - \frac{W_i^{\text{calc}}}{W_i^{\text{obs}}}\right]^2, \qquad (2)$$

was minimized. In it, W_i^{obs} is the observed spectrum and W_i^{calc} is the calculated one; M is the number of spectral channels.

To make a selection of channels from the considered spectral intervals, we analyzed the weighting functions of the direct model:

$$K_{ij} = \frac{\partial W_i^{\text{calc}}}{\partial X_j}, \quad K_{ij}^{*} = \frac{\partial W_i^{\text{calc}}}{\partial(\ln X_j)} = \frac{\partial W_i^{\text{calc}}}{\partial X_j} X_j, \qquad (3)$$

where X_j is the atmospheric parameter sought in the jth node of the vertical grid. For the humidity profile, we used the logarithm of water vapor concentration and logarithmic weighting functions of K_{ij}^{*} type, which allowed us to obtain more homogeneous vertical distribution of a set of logarithmic weighting functions than in the case of direct use of ppm units.

To simulate the spectra like those measured with the IMG device, we used the latest FIRE-ARMS software version,[12] which uses the HITRAN-2004 spectroscopic database[13] and new continuum model MT_CKD for a number of atmospheric gases (http://rtweb.aer.com). The calculations have been performed by solving the radiation transfer equation for outgoing infrared radiation, where the absorption coefficients are calculated line by line.

To reconstruct the profiles of atmospheric parameters, we used the coordinate system of the eigenvectors of the corresponding covariance matrices. The method of reconstructing the vertical temperature and water vapor profiles from high-resolution atmospheric emission spectra employing singular

expansion was suggested earlier and tested using some spectra obtained with IMG/ADEOS and described in Ref. 14. This paper is a continuation of the previous one, where the interrelated *a priori* information is used for profiles of T, H_2O, and HDO, and the method of principal components is applied to obtain the profiles of δD. The method was verified using large selection of IMG/ADEOS spectra measured over the region between 65°S and 65°N and 130 to 170°W.

The quality assessment of *a priori* set of parameter profiles can be done using the condition number of the covariance matrix (ratio between the smallest and largest eigenvalue). For the set of atmospheric states in the considered geographical region, the condition number of the covariance matrices of temperature, concentration logarithms of water vapor, and δD were of the order of $\sim 10^{-4}$.

The procedure of reconstructing the vertical δD profile from the IMG spectra consists of several steps:

a) Formation of the initial atmospheric state. From a prepared set of atmospheric states, we take those which are geographically and temporally closest to the processed spectrum and approximate them. The results are the profiles of pressure, temperature, water vapor, and δD. Other atmospheric parameters (profiles of other gases) are taken from the model of the standard atmosphere.[15]

b) Rough estimate of water vapor profile. From the interval 2 we isolate narrow spectral intervals around the line centers of water vapor of its primary isotope (see Fig. 1) and reconstruct the water profile by varying it from its initial state as a whole. In these intervals, the spectrum is hardly sensitive to the variations of surface temperature or the Earth radiance or to variations of other gases.

c) Surface-temperature adjustment of spectra and choice of the initial approximation. The surface temperature (T_s) is reconstructed using the spectrum from interval 2. For the Earth's radiance we have chosen the spectral dependence typical of marine surface. The estimates of water vapor profile (step *b*) allow better account of the contribution of water lines and the continuum to this spectral region. Then, the initial state is formed again: this time, from available atmospheric states we select the closest in temperature (at the zero altitude) to T_s and average them.

d) Temperature profile refinement. Using the spectrum from interval 1, we reconstruct the temperature profile along with the variation of CO_2 concentration profile as a whole. From this range, we select the portions where the spectrum is insensitive to surface temperature variations, Earth's radiance, water vapor profile, and to the profiles of other gases.

e) Reconstruction of the primary isotope water profile and HDO, *and calculation of* δD *profile*. The profiles of these gases are reconstructed in interval 2 in the chosen spectral channels with H_2O and HDO lines. Because of a small amount of minor isotopomers ($HO^{16}D$, $HO^{17}D$, $HO^{18}D$, ...) as compared to that of the major one ($HO^{16}H$) we use for estimates of δD the characteristic

$$\delta\mathrm{HDO} = \left(\frac{N_{\mathrm{HDO}} / N_{\mathrm{H_2O}}}{R_{\mathrm{SMOW}}} - 1 \right) \cdot 1000\ ‰, \qquad (4)$$

where N_{HDO} and $N_{\mathrm{H_2O}}$ are the reconstructed concentrations of HDO and H_2O.

Results

The technique considered was applied to the IMG/ADEOS spectra in order to obtain the vertical profile of the isotopic ratio δD and the columnar δD value above the Pacific waters during the period of winter 1996 to summer 1997.

Figure 2 presents the latitudinal contour projection of the vertical profiles of δD after their averaging over the longitude. The profiles reconstructed from the IMG spectra are shown by solid lines and the model profiles by the dashed lines.

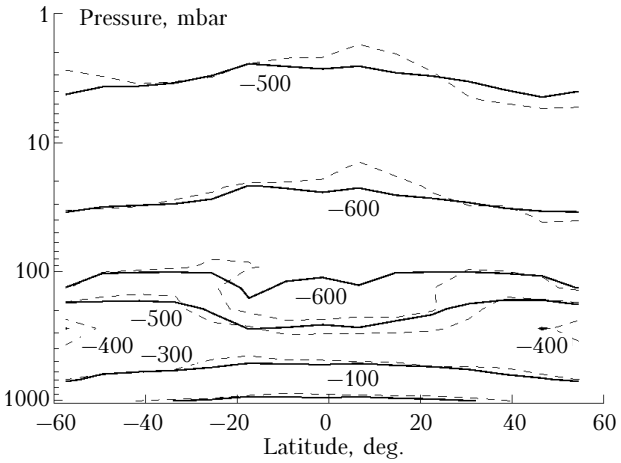

Fig. 2. Latitudinal distribution of the vertical δHDO profile in the atmosphere retrieved by processing the IMG/ADEOS spectra and averaging of the obtained results over longitude. Dashed curves are the contours of the latitudinal δHDO profile in the atmosphere as obtained using general circulation model of the atmosphere for this region and for the mentioned seasons, averaged over longitude.

The value δD in the whole atmospheric column is expressed as

$$\delta\mathrm{HDO}^* = \frac{\int_0^H N_{\mathrm{H_2O}}(h)\,\delta\mathrm{HDO}(h)\,\mathrm{d}h}{\int_0^H N_{\mathrm{H_2O}}(h)\,\mathrm{d}h}\ ‰, \qquad (5)$$

where H is the upper atmospheric boundary. This quantity seems to be quite informative and convenient for representation of the horizontal distribution of the relative deuterium content in the atmosphere. Figure 3 shows the latitudinal distribution of δHDO* calculated from the reconstructed profiles of δD.

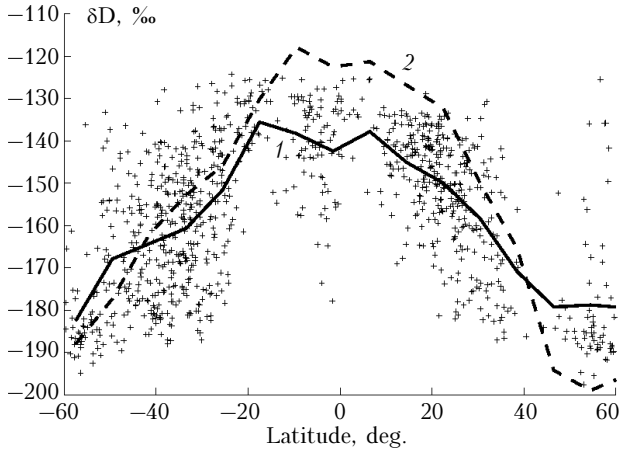

Fig. 3. Latitudinal distribution of δHDO* for the whole atmospheric column obtained from the spectra of IMG/ADEOS (crosses); zonal average of this data over 5° latitude intervals (*1*); zonal average of model data for δHDO* (*2*).

Error analysis

The assessment of accuracy of our method of reconstruction of deuterium content was done using series of model experiments due to the lack of *in situ* data on atmospheric deuterium content in the considered geographical region. In so doing, we have taken the following steps.

1) From a set of model atmospheric states we have made a selection where the characteristic δHDO* for the profiles of δD assumes a sequence of values from −300 to −50‰. The selection made up about 400 atmospheric states.

2) For the selected atmospheres, using the FIRE-ARMS software, we have calculated the fragments of the IMG-type infrared spectra (using the convolution function of the corresponding type and width) that involved the spectral intervals required by the reconstruction method. These spectra were completed with the noise level typical of the measured IMG spectra ($3.5 \cdot 10^{-4}$ W/(m$^2 \cdot$cm$^{-1} \cdot$sr)).

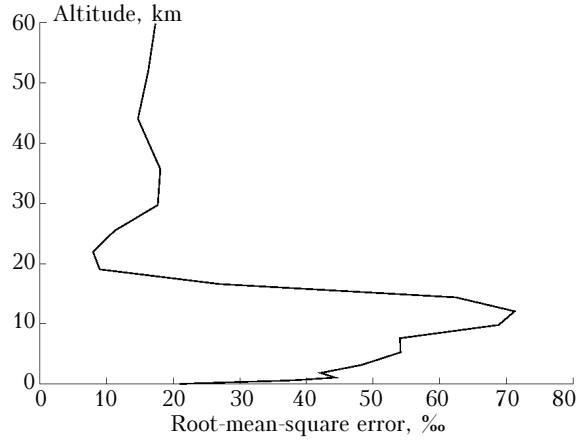

Fig. 4. The root-mean-square error in the method of reconstructing the vertical δD profile obtained from the model experiments with IMG synthetic spectra.

3) Reconstruction of the δD profiles from model spectra using this method and comparison of the results with the original (known) profiles. Calculation of the root-mean-square deviation.

Figure 4 shows the obtained root-mean-square errors of construction of the vertical δD profile using this method. The mean error over the profile kept within 25‰, and the mean error for the relative HDO columnar value did not exceed 20‰.

Conclusion

We have developed and tested the method of reconstructing the vertical profiles of isotopic ratio δD in the atmosphere using *a priori* information, namely, the data calculated using general circulation model of the atmosphere. Having processed the IMG/ADEOS spectra, we obtained the distribution of the vertical profiles and the total atmospheric deuterium content for the geographical region above the Pacific Ocean (65°S – 65°N, 130–170°W). Error analysis in closed experiments with synthetic IMG spectra proved sufficient accuracy of the method for such applications.

The results on reconstructed δD profiles agree with the literature data on the vertical deuterium distribution in the atmosphere and with the calculated data obtained using general circulation model of the atmosphere for this region of the Pacific Ocean. The latitudinal distribution obtained for the total HDO content agrees with the results of our earlier study on IMG/ADEOS spectra processing[9] as well as with recent results of TES spectra processing.[16] The obtained latitudinal deuterium distribution data reconstructed from the IMG spectra can be regarded just as a general assessment of average seasonal HDO content in the atmosphere of this region. The IMG/ADEOS sensor did not provide a dense global daily coverage, so we had to take a variety of irregular data found for the clear sky conditions in the period of winter 1996 – summer 1997. In principle, the technique proposed allows real time processing of IR atmospheric spectra and, with periodical data available about a certain region, it can be used for rapid tracing of air mass transfer or other problems in meteorology and geophysics.

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