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Model Assessment of Atmospheric Precipitation Acidification in the 20th Century Due to Anthropogenic Sulfur Compounds

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Abstract—The acidity of precipitation has been analyzed by calculations with the ChAP-1.0 atmospheric sulfur cycle scheme (Chemistry and Aerosol Processes) developed for the Earth Systems Models of Intermediate Complexity (EMICs) when setting average monthly sulfur dioxide anthropogenic emissions into the atmosphere in 1850–2000 according to the CMIP5 (Coupled Models Intercomparison Project, phase 5) project data and the fields of meteorological variables according to the long-term averages (taking into account the annual variation) of ERA-Interim reanalysis data for 1979–2015. It is revealed that the significant acidity of precipitation (minimum pH of hydrometeors) is typical for regions with a high intensity of anthropogenic emissions of sulfur compounds into the atmosphere—Europe, Southeast Asia, eastern North America, southern Africa and, western South America. In these regions, in the last decades of the 20th century, the typical pH values of precipitation range from 2.5 up to 3.5, which is in good agreement with the available measurement data. The maximum acidity of precipitation (the minimum pH value of hydrometeors close to 2) due to anthropogenic sulfur compounds was noted in the east of the Mediterranean region. The transport of impurities in the atmosphere leads to the fact that, in the last decades of the 20th century, regions with pH < 3.5 cover almost all of Eurasia. The influence of this transfer is also noticeable in other regions of middle latitudes—in the south of North America and in the west of South America. In general, the use of the ChAP scheme is reasonable for the EMICs, but after refinement, taking into account the effect of different types of precipitation on the wet deposition of sulfur compounds from the atmosphere and accounting for the effect of orography on the transport of impurities in the atmosphere.

Keywords: sulfur cycle, sulfates, sulfur dioxide, precipitation, acidity, intermediate complexity models

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1. INTRODUCTION

One component of the anthropogenic impact on the Earth system is the emission of sulfur compounds into the atmosphere. The main contribution to these emissions is sulfur dioxide [1–3]. In the atmosphere, this gas is oxidized to sulfate aerosols (we also note that some anthropogenic sulfates are primary aerosols), which are then removed from the atmosphere by wet and dry deposition. Wet deposition (washout by atmospheric hydrometeors), in turn, leads to the formation of acid precipitation.

Such precipitation in itself is an undesirable natural phenomenon. In particular, they lead to an increase in the acidity of water bodies on land (lakes, rivers, etc.) [4–7], the acidification of soils with degradation of vegetation [8, 9], and the corrosion of steel structures [3]. Note that an increase in the acidity of land water bodies and acidification of soils can also occur during the dry precipitation of sulfates and sulfur dioxide due to their absorption by river or lake water or soil moisture, followed by the inclusion in the chain of sulfur cycle liquid-phase reactions [3, 8].

Traditionally, the characteristic of the acidity of precipitation is pH. In accordance with the definition of the International Union of Pure and Applied Chemistry (IUPAC), this value is determined through the activity of free hydrogen ions in sediments a_{H^+} [10]:

$$\mathrm{pH} = -\log_{10} a_{\mathrm{H}^+} = -\log_{10} \frac{m_{\mathrm{H}^+}\gamma_{\mathrm{H}^+}}{m_\star}; \tag{1}$$

where m_{H^+} is the molality of hydrogen ions in sediments, γ_{H^+} is the activity coefficient of hydrogen ions, and $m_e = 1$ mol/kg. For weak solutions of $\gamma_{\mathrm{H}^+} \to 1$, in connection with which in (1) the so-called approximation of free hydrogen is used [6, 7],

$$pH_F = -\log_{10}\left(m_{\mathrm{H}^+}/m_\star\right). \tag{2}$$

Precipitation acidity measurements are quite rare. This is due, in particular, to the difficulties in isolating various chemicals that affect the acidity of precipitation [6, 11]. Systematic measurements are carried out at several dozen measuring stations over land (see Fig. 15 from [6]). Typical pH values range from 3 to 6, and in some regions even from 2 to 3 [6].

Nevertheless, precipitation acidity can also serve and as an additional tool for verifying models of chemical processes in the atmosphere. In this work, such a verification is carried out for the ChAP-1.0 (Chemistry and Aerosol Processes) scheme for calculating sulfur compounds in the troposphere, developed by the authors of this article.

2. SCHEME FOR CALCULATING THE CONTENT OF SULFUR COMPOUNDS IN THE ATMOSPHERE

A detailed description of the ChAP-1.0 scheme is given in [12]. It has been developed for Earth Systems Models of Intermediate Complexity (EMICs) [13] and allows one to calculate the characteristics of the sulfur cycle in the troposphere. The main assumptions of this scheme are

- Vertical profiles of sulfur compounds X into the troposphere are exponential [2, 14, 15] with height scale H_X; for sulfur dioxide $H_{SO_2} = 1.2$ km and for sulfates $H_{SO_2} = 1.8$ km.
- Nonstationary terms in the balance equations are not taken into account (this is due to the typical formulation of the Earth Systems Models of Intermediate Complexity).
- All chemical reactions obey first order kinetics [1–3]; gas-phase reactions of SO_2 oxidation are not taken into account. The rate constants of heterophase (intracloud (IC)) oxidation depend on the temperature of the lower troposphere and on the proportion of the model cell covered by clouds.
- Wet deposition is taken into account only for sulphates and dry deposition for both SO_2 and SO_4; the intensity of both processes is proportional to the content of the corresponding substance in the atmosphere; for wet deposition, the proportionality constant depends on the temperature of the lower troposphere and on the amount of precipitation.
- The current version of the ChAP-1.0 scheme takes into account only the anthropogenic part of the atmospheric sulfur cycle (this excludes, for example, the formation of sulfur dioxide from dimethyl sulfide and from carbonyl sulfide).

Calculations with the scheme were performed when setting average monthly anthropogenic emissions of sulfur dioxide into the atmosphere in 1850–2000 (in the form of time slices with a time step of 10 years) according to CMIP5 (Coupled Models Intercomparison Project, phase 5) data [16], and the fields of meteorological variables (temperature, precipitation, wind, cloud amount) according to long-term averages (taking into account the annual course) of ERA-Interim reanalysis data [17] for 1979–2015. Failing to account for the interannual and longer term variability leads to the exclusion of feedback between climate and the sulfur cycle of the atmosphere. However, this approach is similar to that used in the preparation of fields for the intensity of anthropogenic and natural emissions of sulfur compounds in the CMIP5 project [16], and therefore it is also used in this work. All calculations were carried out on a computational grid with a step of 4.5° in latitude and 6.0° in longitude, which corresponds to the grid of the earth system model of the Obukhov Institute of Atmospheric Physics of the Russian Academy of Sciences [18, 19].

Note that the total sulfate content per unit area is also available in the CMIP5 data (also obtained without feedbacks accounting for interannual and longer term climate changes), which makes it possible to verify the ChAP scheme [12].

3. PRECIPITATION pH CALCULATION

Because in the ChAP used version, the pH of precipitation is not calculated, in this work the following scheme for calculating this variable is used.

At the rate of wet deposition of sulfate ions $D_{SO_4,\mathrm{wet}}$, the corresponding molar sulfur flux to the surface

$$M_{SO_4} = \frac{D_{SO_4,\mathrm{wet}}}{\mu_S}; \tag{3}$$

where $\mu_S = 32 \times 10^{-3}$ kg/mol is the molar mass of sulfur. With precipitation P and assuming the dominance of sulfate ions from sulfuric acid, this leads to the titration concentration (mol/L)

$$[H_2SO_4]_T = 10^{-3} \times \frac{M_{SO_4}}{\mu_S P}. \tag{4}$$

When exposed to water, sulfuric acid is involved in a chain of reactions

$$\begin{aligned} H_2SO_4 &\rightleftharpoons H^+ + HSO_4^-; \\ HSO_4^- &\rightleftharpoons H^+ + SO_4^{2-}. \end{aligned} \tag{5}$$

As a rule, the main role is played by the first chain reaction (5) with the dissociation constant $K_{H_2SO_4} = 1 \times 10^3$ mol/L [3]. Consequently,

$$\left[H^+\right]\left[HSO_4^-\right] = K_{H_2SO_4}[H_2SO_4]; \tag{6}$$

where $[H_2SO_4]$ is the concentration of undissociated sulfuric acid. Taking into account the law of conservation of mass of sulfur

$$\left[HSO_4^-\right] + [H_2SO_4] = [H_2SO_4]_T, \tag{7}$$

we have

$$\left[\mathrm{H}^+\right]\left[\mathrm{HSO}_4^-\right] = K_{\mathrm{H_2SO_4}}\left[\mathrm{H_2SO_4}\right]_\mathrm{T} - K_{\mathrm{H_2SO_4}}\left[\mathrm{HSO}_4^-\right]. \quad (8)$$

Since, neglecting the second reaction of the chain (5) from the equation of the first reaction of the same chain, it follows that

$$\left[\mathrm{H}^+\right] = \left[\mathrm{HSO}_4^-\right]; \quad (9)$$

then

$$\left[\mathrm{H}^+\right]^2 + K_{\mathrm{H_2SO_4}}\left[\mathrm{H}^+\right] - K_{\mathrm{H_2SO_4}}\left[\mathrm{H_2SO_4}\right]_\mathrm{T} = 0. \quad (10)$$

The only positive root of the last equation is

$$\left[\mathrm{H}^+\right]_\mathrm{S} = \frac{\sqrt{K_{\mathrm{H_2SO_4}}^2 + 4K_{\mathrm{H_2SO_4}}\left[\mathrm{H_2SO_4}\right]_\mathrm{T}} - K_{\mathrm{H_2SO_4}}}{2} \quad (11)$$

$$= \frac{K_{\mathrm{H_2SO_4}}}{2}\left(\sqrt{1 + 4\left[\mathrm{H_2SO_4}\right]_\mathrm{T}/K_{\mathrm{H_2SO_4}}} - 1\right). \quad (12)$$

In view of the self-dissociation of water, which leads to the background value pH_0 7 [3], the corresponding value of the concentration of hydrogen ions $[\mathrm{H}^+]_0$ was added to the solution (12) so that the total concentration

$$\left[\mathrm{H}^+\right] = \left[\mathrm{H}^+\right]_\mathrm{S} + \left[\mathrm{H}^+\right]_0. \quad (13)$$

The acidity of precipitation pH was further calculated by the formula (2).

Setting of numerical experiments in this work with the assignment of meteorological fields in the form of average long-term values excludes the influence of climate change on the characteristics of precipitation acidification. The main effect of this influence is the dependence of the efficiency of sulfate removal from the atmosphere on the type of precipitation, so that, per unit mass of precipitation, the intensity of removal decreases from large-scale liquid precipitation to convective and, further, to large-scale solid precipitation [20, 21]. For the simplest account of this effect, along with basic calculations, calculations were carried out with the exception of precipitation in months with $1/2(T_{850} + T_{1000}) < 0°\mathrm{C}$, where T_{850} and T_{1000} are the temperatures at the isobaric levels of 850 and 1000 hPa, respectively. This excludes precipitation in the form of snow. It should be noted that this approach does not contradict the mass balance of sulfur in the atmosphere reproduced by ChAP; at the same time, in regions and in months with solid precipitation, sulfur compounds are removed from the atmosphere due to dry deposition, and the lifetime of sulfur compounds in the atmosphere increases. However, and even in this case, at the value of the coefficient for dry removal of $\mathrm{SO_4}$ calibrated in [12], it does not exceed 1 month. Thus, on the seasonal time scale (which is analyzed in this article, see below), the mass balance of sulfur in the atmosphere is not disturbed.

4. RESULTS

4.1 Tropospheric Content and Deposition Rates of SO_2 and SO_4

Results of calculations of the content of $\mathrm{SO_2}$ and $\mathrm{SO_4}$ in the troposphere, as well as the intensity of their deposition, are presented in detail in [12]. However, in this work, it is advisable to briefly reproduce them for completeness and convenience in interpreting the results of assessing the acidification of precipitation.

Similar to the results of calculations with other models, globally about half of $\mathrm{SO_2}$ emissions into the atmosphere are converted into sulfates, and the other half is deposited on the earth's surface. The content of anthropogenic sulfur dioxide in the atmosphere increases from zero (according to construction) in 1850 to ≈0.2 TgS in 1970–1990, and then decreases to 0.16 TgS by 2000. At the same time, the mass of anthropogenic sulfates in the atmosphere increases from zero in 1850 to ≈0.4 TgS in 1970–1990 and then decreases to 0.32 TgS by 2000. These values are generally consistent with the CMIP5 estimates. For sulfates, the main role in the model (about 85%) is played by wet deposition, which is generally consistent with estimates based on other schemes of the atmospheric sulfur cycle [22]. The residence time of sulfur dioxide (sulfates) in the atmosphere in ChAP is close to 1 day and that of sulfates is close to 5 days, which also agrees with the results of calculations with other schemes of the sulfur cycle in the atmosphere (see [23] and Table 5.5 from [24]). The global intensity of wet and dry deposition of anthropogenic sulfur compounds from the atmosphere to the earth's surface (with an approximately equal contribution of these types of deposition to total SO_X deposition) is in good agreement with the ACCMIP (Atmospheric Chemistry and Climate Model Intercomparison Project) data [25], in which the influence of interannual and more long-term climate changes on the reproduction of the content of chemicals in the atmosphere was not taken into account as well.

Regional values of the content of both anthropogenic $\mathrm{SO_2}$ and anthropogenic $\mathrm{SO_4}$ are characterized by maxima in the regions of maximum pollution. For the last decades of the 20th century, these are Europe, southeast Asia, and the east of North America. Here, the content of anthropogenic sulfur dioxide and sulfates ($B_{\mathrm{SO_2}}$ and $B_{\mathrm{SO_4}}$, respectively) per unit area is usually ≥2 mgS m^{-2}, and for the last variable it even exceeds 5 mgS m^{-2} (Figs. 3, 5–7 of [12]). In addition, secondary maxima of $B_{\mathrm{SO_2}}$ and $B_{\mathrm{SO_4}}$ are noted in southern Africa and in regions in the west of South

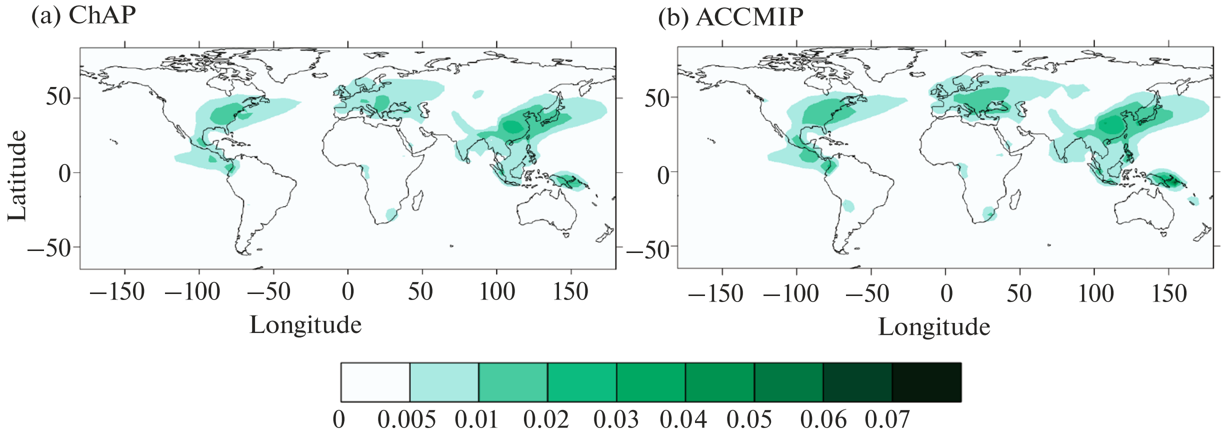

Fig. 1. Wet deposition of SO_X (MgS m^{-2} yr^{-1}) for 2000 according to calculations with the ChAP scheme ((a) only wet deposition of SO_4 is taken into account) and from the results of the ACCMIP project [25] (b).

America. At the same time, the seasonal course of B_{SO_2} in the regions of anthropogenic atmospheric pollution with sulfur compounds is not very pronounced, which is generally consistent with the CMIP5 data. However, according to calculations with ChAP, B_{SO_4} in the same regions is much higher in winter than in summer, which differs from the corresponding CMIP5 data. It should be noted that, even without taking into account the natural emissions of sulfur compounds into the atmosphere, the scheme quite well reproduces at least the average annual B_{SO_4} values in the above regions of anthropogenic atmospheric pollution with sulfur compounds in comparison with the CAMS (Copernicus Atmospheric Monitoring System) reanalysis data [26].

The geographical distribution of the annual total precipitation of anthropogenic sulfur compounds is generally similar to the geographical distribution of anthropogenic emissions of this element.

For the last decades of the 20th century, the total deposition rate (the sum of wet and dry deposition rates) of D_{SO_4} sulfur compounds in the regions of the corresponding anthropogenic atmospheric pollution in the Northern Hemisphere exceeds 2 mgS m^{-2} yr^{-1} (Fig. 1). The spatial distribution of annual D_{SO_4} in the ChAP scheme over the continents is similar to that obtained in the ACCMIP project. However, compared to the ACCMIP data, the ChAP scheme overestimates the intensity of wet deposition and underestimates that of dry deposition. However, in Europe, the agreement for wet deposition improves markedly when using the EMEP MSC-W (Meteorological Synthesizing Centre–West of the European Monitoring and Evaluation Program) data [27] and by calculations with the MOGUNTIA [28], IMAGES [29], and GISS models [22].

4.2 Acidity of Precipitation

For the conditions of 1850, anthropogenic emissions of sulfur dioxide into the atmosphere can significantly change the acidity of precipitation from the background value pH_0 7 (Fig. 2). In particular, in different seasons, pH is in the range from 4.2 to 5.4 in the regions of the most significant pollution with sulfur compounds, primarily over Europe. The acidity of precipitation is most significant in summer. Note that the latter is observed even taking into account the general underestimation of B_{SO_4} in this season by the ChAP scheme. As a result, the effect of precipitation acidification by sulfur compounds for the indicated year may actually be even more pronounced than in our calculations.

The general increase in the intensity of anthropogenic emissions of sulfur compounds into the atmosphere during the 20th century also leads and to a significant increase in precipitation acidification for the last decades of this century (Figs. 3, 4). At the same time, other regions with a high intensity of anthropogenic emissions of sulfur compounds into the atmosphere are added to the European region of significant acidity of precipitation—southeast Asia, eastern North America, southern Africa, and western South America.

For both time slices in these regions, the typical pH values of precipitation range from 2.5 to 3.5. These values are in good agreement with those shown in Fig. 15 from [6] for time intervals 1986–1995 and 1996–2005 (see also Fig. 20.8 from [1]). For the territory of Russian Federation, they also satisfactorily agree with the data of direct observations [30], except for the regions of the Volga and Transbaikal regions, where the acidity of precipitation in the ChAP scheme is higher than according to the observational data. The maximum acidified precipitation (with pH close to 2) in the scheme is reproduced in the east of the Mediterranean

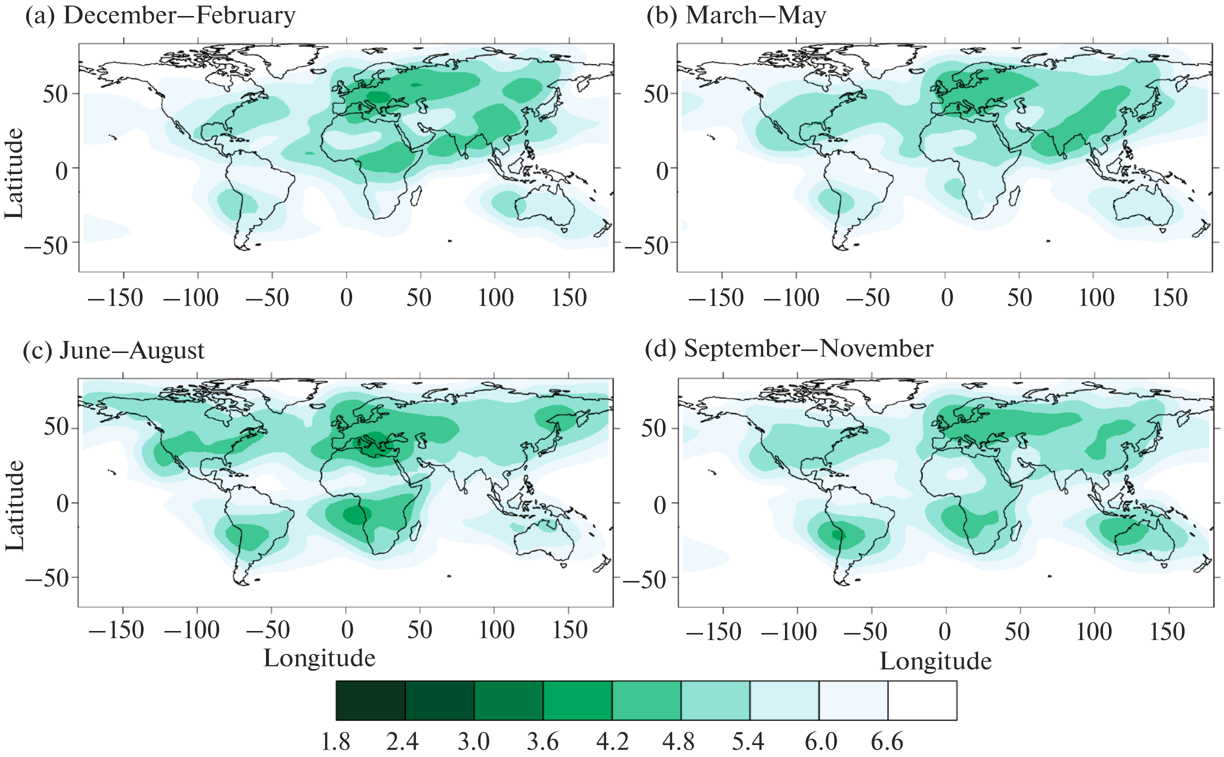

Fig. 2. pH of precipitation for emissions of sulfur compounds into the atmosphere corresponding to 1850 in December–February (a), March–May (b), June–August (c), and September–November (d).

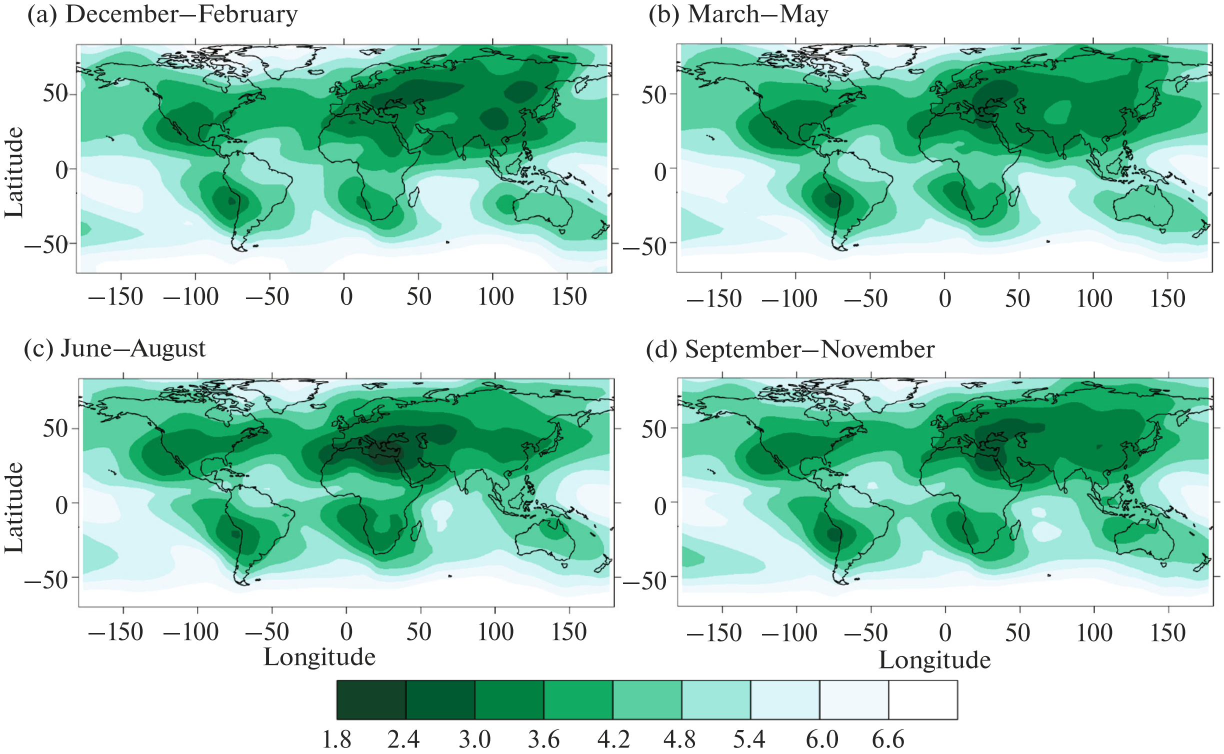

Fig. 3. Similar to Fig. 2, but for emissions of sulfur compounds into the atmosphere corresponding to 1990.

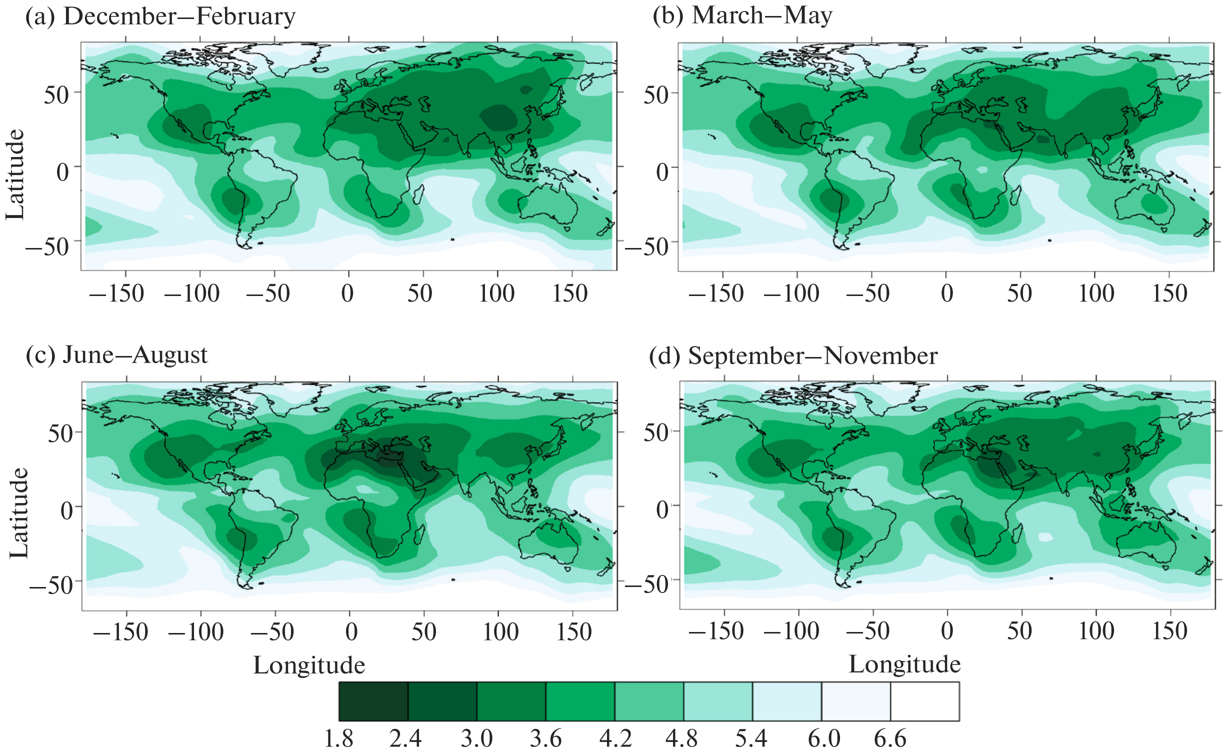

Fig. 4. Similar to Fig. 2, but for emissions of sulfur compounds into the atmosphere corresponding to 2000.

region in summer. It should be noted that, in the same region, the minimum value of pH < 2 was also noted according to systematic observations for 1986–1995. This value does not appear for the later time interval 1996–2005. Taken together, this indicates that the acid precipitation in this region around 1990 is at least partially related to the atmospheric transport of sulfates from Europe. It should be noted that this result is consistent with [31], where it was noted that the transfer of air masses to the European territory of Russian Federation from the Mediterranean is accompanied by an increase in precipitation acidity.

Atmospheric transport also leads to the fact that, in the last decades of the 20th century, regions with pH < 3.5 cover most of Eurasia, southern North America, and western South America. In the Northern Hemisphere, precipitation is more acidic in summer than in winter. This generally agrees with individual measurements in a number of regions [3, 32]. In addition, during the Southern Hemisphere winter, the scheme also reproduces a similar area in southern Africa and over the adjacent part of the Atlantic. It is difficult to compare these calculations with observational data due to the lack of systematic measurements of precipitation acidity outside the regions with a high intensity of anthropogenic sulfur emissions into the atmosphere [6].

It should be noted that the transport of impurities in the atmosphere in the version of the ChAP scheme used in this work does not take into account the effect of orography. The latter can serve as one of the reasons for the underestimation of the acidity of precipitation in the Volga and Transbaikal regions. The first of these regions is predominantly influenced by the European source region, but is separated from it by the Valdai Upland with a height of up to about 400 m. The height of the mountain ridges separating the second region—the Trans-Baikal territory—from the corresponding source region located in southeast Asia is even higher and reaches several kilometers. Thus, the agreement between model calculations and direct observational data in these regions can be improved by taking into account the effect of orography on the transport of impurities in the atmosphere. At the same time, one can also expect an improvement in the reproduction and seasonal variation of the pH of precipitation.

The main difference between the 1900 and 2000 time slices is a general decrease in acidity in Europe and, to a lesser extent, in North America, southern Africa, and South America for the second slice relative to the first, with an increase in South and Southeast Asia. These trends are mainly due to the corresponding trends in anthropogenic sulfur emissions into the atmosphere in these regions [2]. In the regions of Eurasia, subject to pollution by sulfur compounds from the European region, the decrease in precipitation acidity is most significant in winter and spring. For other regions that show a decrease in precipitation

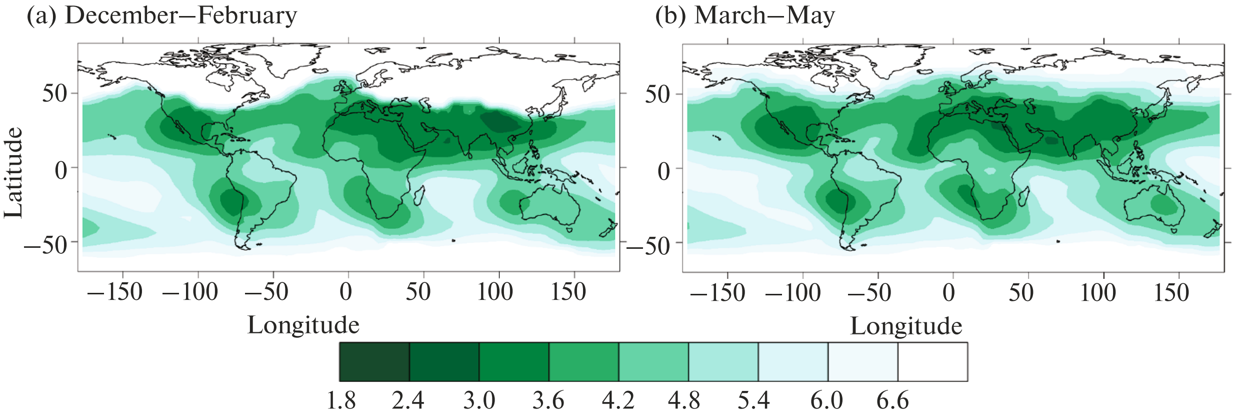

Fig. 5. Similar to Figs. 4a and 4b, but excluding solid precipitation.

acidity, this decrease is more uniformly distributed over the calendar seasons. The increase in precipitation acidity from 1900 to 2000 in southern and southeastern Asia is also relatively uniform in seasons.

4.3 Sensitivity of Precipitation Acidity to Precipitation Type

The setup of numerical experiments described above makes it difficult to fully analyze the sensitivity of pH to the type of precipitation (large-scale liquid, large-scale solid, and convective). However, the simplest analysis can be carried out by excluding the most inefficient type of precipitation for wet washout—snow. The corresponding analysis was carried out with the exclusion of such precipitation in accordance with the algorithm of Section 3. Note, however, that such an approach is very rough. For example, it does not take into account the winter thaws with possible large-scale precipitation of low intensity (which, in terms of a unit mass of falling moisture, is most effective for the wet removal of sulfur compounds in the atmosphere [20, 21]) or, conversely, the development of severe storms in transitional seasons with precipitation in the form of snow. An adequate analysis of such effects is possible only if the type of precipitation is taken into account, which is difficult in this work. Nevertheless, the rough approach used in this work to account for the influence is reasonable, especially in view of the general overestimation of the content of sulfates in the atmosphere by the ChAP scheme in winter.

Since such an approach obviously should not affect the pH of precipitation in summer, it is sufficient to restrict ourselves to the winter period (Fig. 5a) and transitional periods (for example, in spring; Fig. 5b). At the same time, in both cases, in regions with negative temperatures in the lower troposphere, the acidity of precipitation decreases significantly. This agrees with review [6] of the results of measuring the pH of hydrometeors.

5. DISCUSSIONS AND CONCLUSIONS

In this work, we analyzed the acidity of precipitation according to calculations with the ChAP-1.0 atmospheric sulfur cycle scheme (Chemistry and Aerosol Processes) developed for models of the Earth system of intermediate complexity. Calculations with this scheme were performed when setting average monthly anthropogenic emissions of sulfur dioxide into the atmosphere in 1850–2000 (in the form of time slices with a time step of 10 years) according to the data of the CMIP5 project (Coupled Models Intercomparison Project, phase 5) and the fields of meteorological variables according to long-term averages (taking into account the annual course) of ERA-Interim reanalysis data for 1979–2015. Calculations were carried out on a grid with a step of 4.5° in latitude and 6.0° in longitude.

It was revealed that significant acidity of precipitation is typical for regions with a high intensity of anthropogenic emissions of sulfur compounds into the atmosphere—Europe, Southeast Asia, eastern North America, southern Africa and western South America. In these regions, in the last decades of the 20th century, the typical pH values of precipitation range from 2.5 up to 3.5, which is in good agreement with the available measurement data. The maximum acidity of precipitation (the minimum pH value of hydrometeors close to 2) due to anthropogenic sulfur compounds was noted in the east of the Mediterranean region. In the Northern Hemisphere, precipitation is more acidic in summer than in winter. The transport of impurities in the atmosphere leads to the fact that, in the last decades of the 20th century, regions with pH < 3.5 cover almost all of Eurasia. The influence of this transfer is also noticeable in other regions of middle latitudes—in the south of North America and in the west of South America. Nevertheless, a number of differences in the spatial distribution of the model data from the data of direct measurements, as well as the corresponding differences in the seasonal course, can be associated with the neglect of the effect of orography on the transport of pollutants in the atmosphere in the version of the ChAP scheme used in this work.

It should be noted that the increase in the size of regions prone to acid precipitation compared with the size of the source region can be estimated precisely as a consequence of transport in the atmosphere. If we assume that

- most of the anthropogenic emissions of sulfur into the atmosphere occur in the form of sulfur dioxide, followed by its oxidation to sulfates, which are removed from the atmosphere mainly by wet deposition;
- the size of sulfur dioxide source regions is negligible compared to the size of the region of influence of this source; then the order of magnitude of the size of the region affected by the source in the direction of the prevailing wind speed u can be estimated as follows:

$$L = u\left(\tau_{SO_2} + \tau_{SO_4}\right); \tag{14}$$

where τ_{SO_2} and τ_{SO_4} are the lifetimes in an atmosphere of sulfur dioxide and sulfates, respectively. Taking into account the typical wind speed at middle latitudes in the lower troposphere ≈5 m/s [12] and typical values of $\tau_{SO_2} \approx 1$ day and $\tau_{SO_4} \approx 5–6$ days (see [1–3, 23] and Table 5.5 from [24]), this leads to the estimate $L \simeq (0.5 - 1) \times 10^4$ km, which is comparable to the size of Eurasia (16 000 km from west to east). Considering the size of the European region as source, which is several thousand kilometers (this value should be added to the L estimate at a rough estimate), this generally explains the effect of the European region as source on the acidity of precipitation over all of Eurasia.

We also note a number of limitations of this work.

- This work does not take into account natural emissions of sulfur compounds—primarily dimethyl sulfide from the ocean surface and the release of sulfur dioxide and sulfates from volcanoes. The current intensity of the first source is estimated at about 28 TgS/year [33–35]; the second one is about 23 TgS/year (the release of sulfur dioxide due to eruptions is an order of magnitude less) [36]. The total intensity of these sources is comparable to the intensity of anthropogenic SO_2 emissions into the atmosphere in the last decades of the 20th century (≈54 TgS/year [37]). Thus, taking them into account can additionally increase the acidity of precipitation, including over the continents. Taking into account the logarithmic dependence of pH on the concentration of hydrogen ions in hydrometeors, this increase can lead to a decrease in pH by several tenths.
- Precipitation acidity can also increase when the wet deposition of sulfur dioxide is taken into account. However, for most modern models, the contribution of wet deposition of SO_2 to the total deposition of this gas does not exceed 15% [24], which will only slightly change the pH values calculated in this work.
- This work does not take into account the influence on the pH of sediments of bases of other acids present in the atmosphere (including nitric acid). In connection with the latter, it is important to bear in mind, that after 2000, in industrially developed regions (Europe, the United States, and China), an increase in the content of nitrates in precipitation was noted [11]. It is difficult to make an adequate assessment of this effect in this work. However, based on the general realism of the results obtained and their satisfactory agreement with the available observational data, it can be argued that, for the spatiotemporal resolution used in this work, the inclusion of such substances will not change the pH of sediments by more than one. In addition, the period with an increase in the contribution of nitrates to the precipitation acidity is not taken into account in this work, because calculations end in 2000.
- In addition, this work does not take into account the effect of carbon dioxide on precipitation acidity [1–3]. Being well mixed in the atmosphere, carbon dioxide is able to reduce the spatial differences in pH between regions with high and low atmospheric pollution by sulfur compounds.

Thus, the additional verification of the ChAP scheme carried out in this work shows its realism for models of the earth system of intermediate complexity. In this case, however, it is advisable to refine the scheme, taking into account the effect of precipitation of various types on the wet deposition of sulfur compounds from the atmosphere and taking into account the effect of orography on the transport of impurities in the atmosphere.

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CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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