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Simulation of spatial distribution of the sea bottom methane hydrates and estimates of the methane fluxes into the atmosphere*

V.V. Malakhova, A.V. Scherbakov

Abstract. The estimate of the methane emission from hydrates is based on the data indicating to the location and potential thickness of the hydrate stability zone. Gas hydrate abundance in the marine sediment depends on the gas concentration and the available pore space within certain stability limits. In this paper, we establish the methane ocean environment, based on the latitudinal distribution of the methane hydrate stability zone, for a range of geothermal gradients and sediment porosities. The possibility of the methane hydrate decomposition due to the global climate changes is investigated using the world ocean model. It is supposed that the temperature of the ocean surface rises up to 1.5 degree during 50 years and then decreases to 1.5 degree. The climatic model, supplemented with a one-dimensional model of a bottom sedimentary layer of the ocean, is integrated for a period of 2000 years and simulates penetrations of warming from the surface deep into the ocean and sediments. A three-dimensional equation of transport of dissolved methane from sources is simultaneously solved. The methane flux into the atmosphere has reached 2 Tg/year.

Methane is a greenhouse gas which is twenty times more effective than CO_2, but its concentration is smaller. The methane concentration in the atmosphere is increasing at a rate of about 1–2 % a year, from 0.8 ppm in 1840 to 1.7 ppm today (as compared with CO_2, which rose from 280 to 370 ppm), [1].

While much of the oceanic methane arriving at the seafloor is converted into oxide,carbonate, sulfide and organic matter, which is eaten by clams, snails, bacteria and other organisms, some of it is in the form of a free gas, dissolved gas or hydrate, and arrives at the seafloor, where it floats upwards. But what quantity of free gas reaches the surface is unknown. Most of it should rise, being dissolved in the upwelling currents, because the solubility declines sharply at the surface, [2].

One of largest potential sources of the methane emission to the atmosphere is natural gas hydrates. Gas-hydrate deposits occur under specific conditions of pressure and temperature, where the supply of methane is sufficient to initiate its formation. These conditions exist on the Earth in the upper 2000 m of sediments in the two regions: (1) continental, including

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continental shelves, at high latitudes in the polar regions, where the surface temperatures is very law (less than 0 °C) and (2) submarine continental slopes and rises, where the bottom water is cold and pressures are high (exceeding 3 MPa), [4].

Gas hydrate is found at water depths greater than 300–500 m, depending on the bottom-water temperatures. The quantity estimations of methane, which can reach the atmosphere by melting methane hydrates, and the time scale of this phenomenon, are the key parameters in this case. Gas hydrates are crystalline substances composed of gas and water that are stable at high pressure, low temperature, and high gas concentration. Enormous quantities of methane are stored as gas hydrate and free gas bubbles in the upper several hundred meters of sediments on many continental margins, [3]. The amount of methane sequestered in gas hydrate is undoubtedly very large, probably greater than 10^{15} m^3, but, less than 10^{17} m^3, [4]. The maximum amount of methane that can be accommodated in methane hydrate is fixed by the crystal structure at $CH_4 \cdot 5.75H_2O$. Methane hydrate can therefore contain as much as 164 times its own volume of methane at standard temperature and pressure, [3].

In the previous works, [5, 6], the problem of possible consequences of the destabilization of methane hydrates which contact with the seawater under an increase in the surface ocean temperature was considered. It was supposed that methane hydrates exist at the bottom and at the continental slope everywhere, where the pressure-temperature conditions of their stability are valid. As soon as warming from the ocean surface reaches some near bottom waters and raises their temperature to definite value-tolerance, [8], the destabilization of methane hydrates begins. In the model, the destabilization is set as an increase in concentration of methane at a near bottom grid point. It appears that at such assumptions the time interval from the beginning of the surface water warming to the beginning of a possible destabilization is small, about several years because in high latitudes the warming from the surface waters due to the vertical convection quickly reaches the near bottom waters.

The data on distribution of the ocean methane hydrates show that as a rule they lie in a sedimentary layer at subbottom about hundreds meters depths. Therefore, to decompose methane hydrates, there is needed a penetration of warming not only to the bottom, but also into a sedimentary layer, which demands a greater time as compared to the case of methane hydrates contacting directly with water. In [7], a model of methane with a sedimentary 1000 meter bottom layer was considered. Any estimates of future rates of methane release into the atmosphere require more information on their spatial distribution. In this paper, we consider a methane ocean environment, based on the latitudinal distribution of the methane hydrate stability zone, for a range of geothermal gradients and sediment porosities.

The climatic state of the ocean was obtained from the three-dimensional World ocean model including the seasonal variability, with a real bottom topography, [9]. The problem was solved on the whole test site of the World ocean on the five-degree latitude-longitude grid from 72.5° S up to 87.5° N with 24 vertical levels till the stationary state through the time about several thousands years, [10].

The ocean model is supplemented with a one-dimensional model of a bottom sedimentary layer

$$\frac{\partial T_s}{\partial t} = \frac{\partial}{\partial z} \varkappa_s \frac{\partial T_s}{\partial z} \tag{1}$$

with boundary conditions

$$z = H : \qquad T_s = T_{s,b}, \tag{2}$$

$$z = H + d : \qquad \varkappa_s \frac{\partial T_s}{\partial z} = Q_t, \tag{3}$$

$$t = 0 : \qquad T_s = T_{s,\text{climate}}(z). \tag{4}$$

Here $\varkappa_s = 10^{-2}$ cm/s is the conductivity coefficient of the sedimentary layer; Q_t is the geothermic heat flux; T_s is the temperature of the sedimentary layer; $T_{s,b}(z)$ is the temperature in the ocean bottom from climate model,[10]; $T_{s,\text{climate}}(z)$ is the solution to the stationary equation (1) with the climatic temperature from climate model, [10].

The governing equations (1) is solved in a discretized form assuming a uniform grid spacing of 20 m and time differencing with 10-day time steps. The bottom of the model is placed at a depth of $d = 1000$ m below the sea level.

Advective-diffusion process of transport of the dissolved methane in sea water, which concentration we shall designate by the letter C, we shall describe by the equation

$$\frac{\partial C}{\partial t} + \frac{u}{a \sin\theta} \frac{\partial C}{\partial \lambda} + \frac{v}{a} \frac{\partial C}{\partial \theta} + w \frac{\partial C}{\partial z} = \frac{\partial}{\partial z} \varkappa \frac{\partial C}{\partial z} + \frac{\mu}{a^2} \Delta C,$$

with boundary conditions

$$z = 0 : \qquad C = C^*(\lambda, \theta),$$

$$z = H : \qquad \varkappa \frac{\partial C}{\partial z} = 0,$$

$$\text{on } \Gamma : \qquad \mu \frac{\partial C}{\partial n} = 0.$$

Here C is concentration of the dissolved methane. The methane concentration on a surface of ocean was set the distribution, depending only from a latitude was given: $C^*(\theta) = (1 + \cos\theta) \cdot 50$ ppb, which zonally change from 50 ppb in southern high-latitude areas of the ocean up to 100 ppb in the northern high-latitude areas, 1 ppb $= 10^6$ ml/l.

The following notations are used: u, v, w are velocity vector components on the coordinates λ, θ, z, where λ is longitude, θ is an addition of the longitude up to 90°, z is directed vertically downwards; t is time; $H(\lambda, \theta)$ is the bottom relief, $\varkappa$ and μ are the vertical and horizontal turbulent temperature and salinity diffusion coefficient.

Numerical experiments began with the same initial calculated climatic fields. Gas hydrate abundance in the marine sediment depends on gas concentration and the available pore space within certain stability limits. It is supposed that methane hydrates exist in a sedimentary layer, where the pressure-temperature conditions of their stability are valid. We take into account the gas hydrate stability curve for the methane sea water system, [11]. The authors proposed an interpolation formula based on their measurements

$$\frac{1}{T_{\text{stab}}} = 3.79 \cdot 10^{-3} - 2.83 \cdot 10^{-4} \log_{10} p_{\text{stab}},$$

where T_{stab} is the stability temperature in K and p_{stab} is the stability pressure in MPa.

Figure 1 illustrates a variation in the critical temperature for methane clathrate destabilization as a function of depth, assuming a hydrostatic increase in pressure. Gas hydrates potentially occur in marine sediment between two bounding surfaces. The “Base HSZ” is a lower limit the gas hydrate distribution regardless of gas concentration. Below this depth, gas will exist dissolved in water or as free gas bubbles. We consider the sea floor to be a maximum upper limit of the gas hydrate distribution.

Although the pressure and temperature conditions are satisfied throughout most of the world oceans, hydrate occurrences are generally restricted to the continental margins where conversion of high inputs of organic carbon. As the water depth increases, and the temperature of the seafloor decreases, the zone of stability becomes thicker. However, clathrate has never been detected in this sediment, because the rate of the carbon rain onto the seafloor is too low to supply a required source of methane through microbial conversion of organic material in the sediments. In fact, 90 of the global carbon burial is thought to occur at a water depth of less than 1000 m, [12]. We do not consider columns of the ocean water at seafloor depths greater than 3000 m, since a significant rise of temperature for destabilization would be required.

The thickness Δz of the hydrate stability zone (HSZ) can be calculated knowing the methane hydrate stability curve, the ocean bottom temperature and the geothermal gradient. Let z_0 be the ocean floor depth. At a given depth z, methane hydrates are available, where $T(z) \le T_{\text{stab}}(z)$.

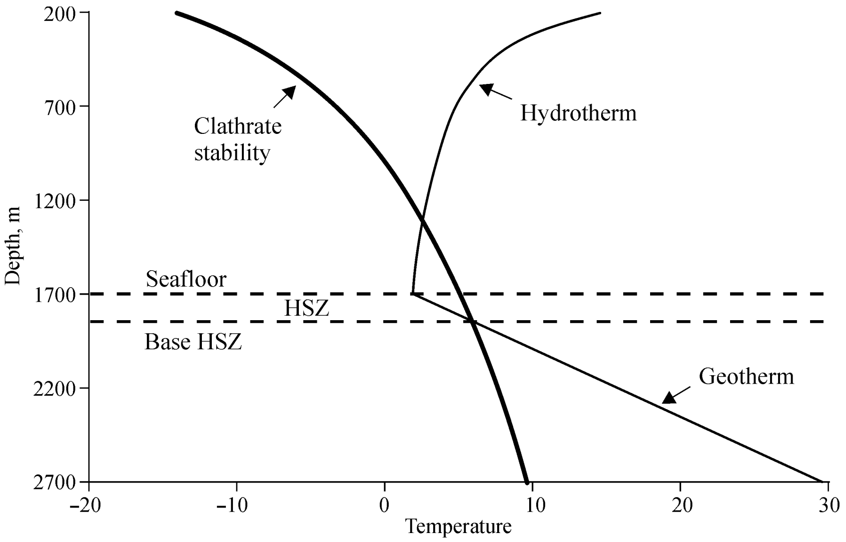

Figure 1. Stability diagram of methane hydrate. The temperature for hydrate stability increases with depth for an assumed water depth of 1700 m, a thermal gradient being 30 °C/km. Under these conditions the hydrate stability zone (HSZ) is 140 m thick

The thickness Δz of the potential stability zone is the depth difference between the top of the HSZ (in our case, this is the seafloor depth) and its base, at the depth, where the sediment temperature exceeds the equilibrium temperature, for a given thermal gradient.

The sediment temperature at the ocean floor, the presence or the absence of a clathrate-stable zone and its thickness strongly depend on the vertical temperature gradient in a sediment, Q_t. In [7], the geothermic heat flux was constant, equal to 30 °C/km. The marine heat flow data used here are obtained from the database providing information on more than 8000 data points from the world ocean, and the thermal gradient calculated for 22 ocean regions, [13, Table 2]. The geothermic heat flux ranges from 30 to 87 °C/km in marine sediments.

Although from the thermodynamic standpoint hydrates are allowed to form anywhere within the zone, this only happens if a sufficient amount of methane gas and water exist. The evidence suggests that hydrates do not occupy the entire zone of stability, but rather exist as layers mainly near the bottom of the stability zone [14]. A decrease in the sediment porosity $P(z)$ can vary linearly or nonlinearly, depending on sediment composition. We assume a simple exponential variation of sediment porosity with a sediment depth, derived from empirical data, [13, 14]:

$$P(z) = P_0 \exp[-(z - z_0)],$$

where $P_0 = 0.72$, [13], is the sediment porosity at the seafloor and L=1500 m is e-folding depth based on [13–15].

The share of the sediment porosity $P_H(z)$ within the HSZ actually contained in gas hydrate is a major uncertainty in deriving the magnitude of the hydrate reservoir. Cores from the North Slope, Alaska, suggest that only 10% of the hydrate stability zone may actually contain hydrates, [13]. We assume that $P_H = P/2$ at $z_{\mathrm{HSZ}} = z_0 + \Delta z$, the base of the HSZ, decreasing linearly to 0 at the sea bottom z_0 as in [14]:

$$P_H(z) = 0.5P(z_{\mathrm{HSZ}})\frac{z - z_0}{z_{\mathrm{HSZ}} - z_0} \cdot 100\ \%, \quad z_0 < z < z_{\mathrm{HSZ}}.$$

For the purpose of calculation of the subbottom sediment depth $H_{\mathrm{hyd}}(\lambda, \theta)$ where methane hydrates lie, we assume that, if $P_H(z) \geq 10\ \%$, then $H_{\mathrm{hyd}}(\lambda, \theta) = z$. As a result of this approach, the defined subbottom depths, where methane hydrates lie, consist of 20 to 320 m of the marine bottom sediment. Distribution of the methane hydrates at a depth of 100 m below the sea level in sediment for model experiments is shown in Figure 2. The methane sources are largely concentrated in the northern hemisphere, 40° N.

The data about paleoclimate [17] show that climatic changes have a periodic character. Warming is replaced by cooling, and the periods of these fluctuations change from tens up to thousands years. The increased ocean surface warming can be transported toward the seafloor. In this paper, scenarios of changes of the surface water temperature both with warming and with cooling for a period of 100 years are considered, [16], using the

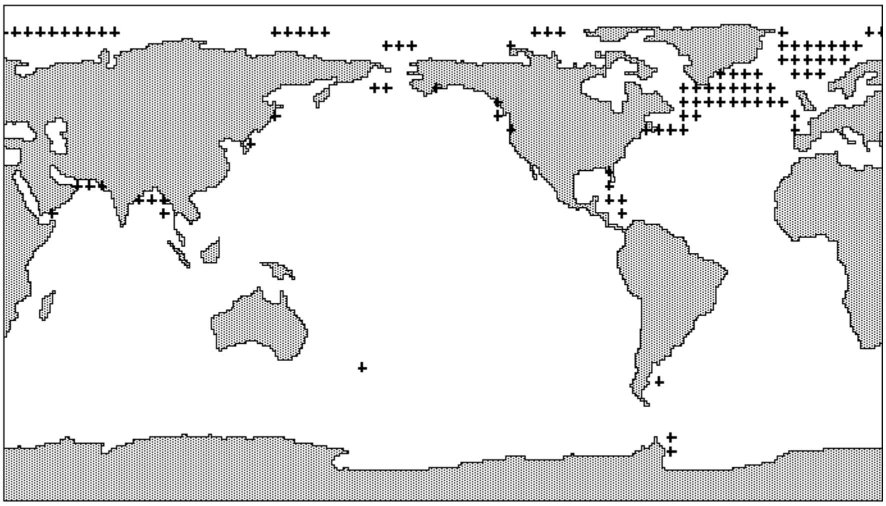

Figure 2. Distribution of the methane hydrates sources on the depth from 20 to 100 m below sea bottom in sediment

coupled ocean–sediment general circulation model, [7]. In each experiment, the time of the beginning of destabilization of methane hydrates, a part of the bottom containing such sources and the diffusive methane flux into the atmosphere are determined.

In the numerical experiments, the seasonally changing surface ocean temperature everywhere, except for the polar areas covered with ice all year, round linearly increases by 1.5 degree for the first 50 years of the experiment and then it also linearly decreases by 1.5 degree up to the initial values, also, for 50 years. Further, the ocean surface temperature continues to vary according to the seasonal climatic data. A thermal signal from the ocean surface by the convective mixing and currents is transported to the deep ocean up to the near bottom layers. Further, with the help of the one-dimensional equation of heat conductivity (1) with conditions (2), (3) an increase in temperature of a sedimentary layer is simulated and compared to the initial climatic values. As soon as this increase exceeds some allowable value — the tolerance [7], which is a parameter of the scenario, for example, $\mathrm{Tol} = 0.01^\circ$, and this also occurs on a certain subbottom depth $H_{\mathrm{hyd}}(\lambda, \theta)$, where methane hydrates lie, it is supposed, that the decomposition of methane hydrates begins. This decomposition supports the near bottom concentration of the dissolved methane equal to 5000 ppb. Thus, it is considered that the methane released by the decomposition is completely dissolved in the sea water. In a sequel, this value is used as boundary condition at this point of the bottom for the solution of the methane transport equation, instead of a zero methane flux. Such an approach proves to be correct according to dates of measurements of methane concentration. Intensive methane fluxes were found on the East Sakhalin shelf in the Okhotsk Sea, [18]. The methane bubbles migrate from the sediment into water and form a flare with methane concentrations inside it more than 20000 ppb and near the flare — about 1000–3000 ppb.

Once methane is released from the hydrate, it may be transported from the sediment to a water column as a dissolved gas by diffusion through sediments or through advection of pore water [19] if the pore waters become supersaturated, methane may also be transported by active bubbling. Methane, dissolved in a deeper water column remains in solution until the water mass equilibrates with the atmosphere. Thus, a source of methane "is switched on" in the model. If further, in the coarse of the experiment, an increment of heat in a sedimentary layer at a methane hydrates depth becomes less than the tolerance Tol, it is supposed, that the destabilization has stopped or, in other words, a source "is switched off". This means that again there is used a boundary condition for the equation of methane transport with a specified value 5000 ppb.

Two experiments with a different subbottom sediment depth of the sources of methane were carried out. In the numerical experiments "Hy-

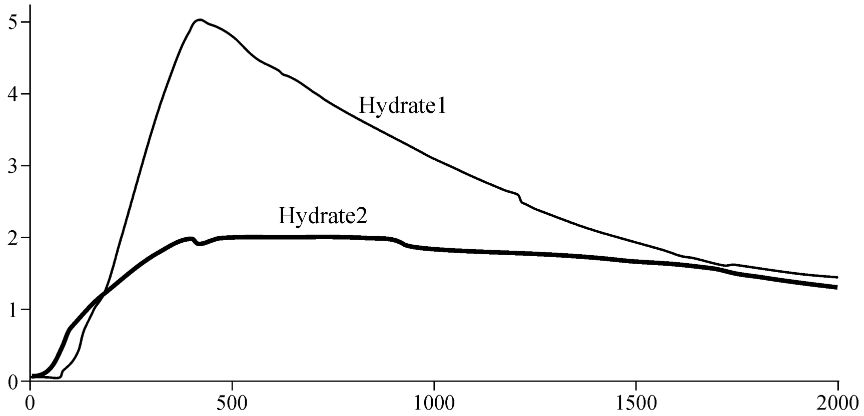

Figure 3. Methane flux into the atmosphere from decomposed methane hydrates, in Tg/year

drate1", the depth of methane hydrates $H_{\text{hyd}} = 100$ m in the Southern and the Arctic oceans and continental shelf and $H_{\text{hyd}} = 300$ m in other oceans, as in [7]. Figure 3 shows the summarized methane flux in the atmosphere as functions of time for a period of 2000 years of integration.

The time before the beginning of the destabilization in the first experiment is about 76 years with the tolerance Tol $= 0.01^\circ$ at the depth of the methane hydrates. The methane flux into the atmosphere reaches its maximum 5 Tg/year after 409 years from the beginning of the experiment "Hydrate1". The sources of methane hydrates "are switched on" on the area of exceeding 11 % of the ocean bottom and provide a maximum of average concentration of the dissolved methane 957 ppb after 492 years.

In the numerical experiments "Hydrate2", the depth of methane hydrates in sediments $H_{\text{hyd}}(\lambda, \theta)$ is calculated depending on geothermal gradients and sediment porosities, see Figure 2. The subbottom depth, where methane hydrates lies, is 20 to 320 m of the marine sediment. The destabilization begins after 10 years from the beginning of the experiment. The sources "are switched on" the area about 6 % of the bottom and provide a maximum of average concentration of the dissolved methane 500 ppb after 1000 years. The maximal methane flux into the atmosphere reaches 2 Tg/year only after 500 years. In Figure 4, the distribution of the dissolved methane concentration at a depth of 250 m after 100 years is shown. We can see that after 100 years of the climate changes, methanhydrates begin decomposing on all the coasts of Arctic and in the Greenland sea. After 400 years, the areas of decomposed methane hydrates increase, Figures 5–6.

Analysis of the calculated dissolved methane concentration in the World ocean, see Figures 4–6, shows that after the beginning of warming the first to destabilize are methane hydrates, which are located at depths up to 1000 m in a sedimentary layer at subbottom depths up to 100 m in high latitudes.

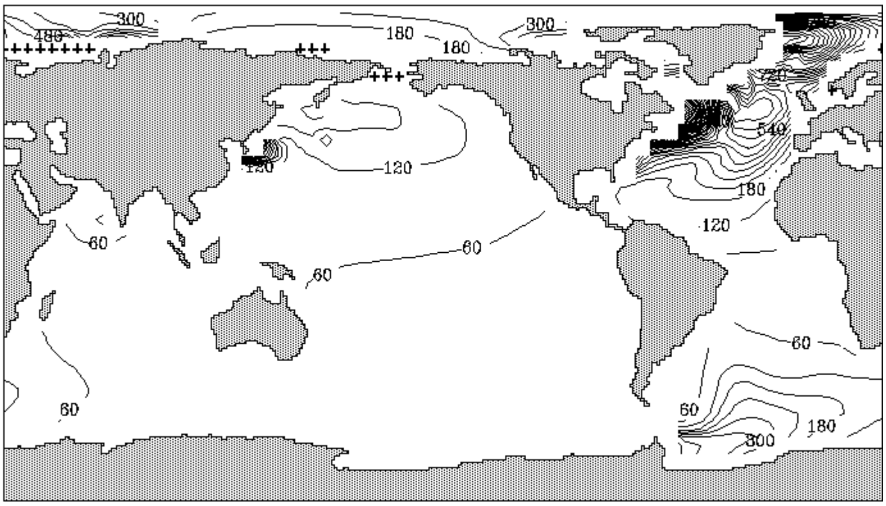

Figure 4. Isolines of dissolved methane at the depth of 250 m in 100 years after the beginning of climate variability in the experiment "Hydrate2". Maximum of methane concentration is 2400 ppb

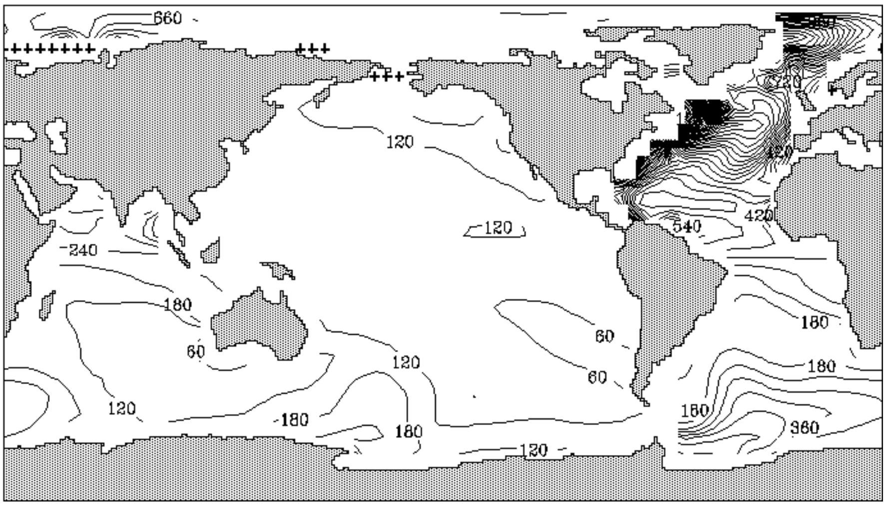

Figure 5. Isolines of dissolved methane at the depth 250 m in 400 years after the beginning of climate variability in experiment "Hydrate2". Maximum of methane concentration is 2800 ppb

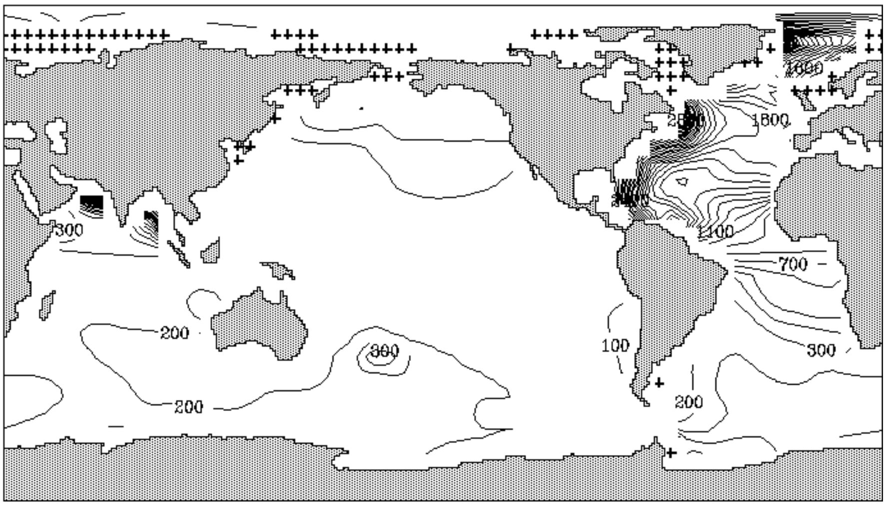

Figure 6. Isolines of dissolved methane at the depth 900 m in 400 years after the beginning of climate variability in experiment “Hydrate2”. Maximum of methane concentration is 4300 ppb

One can see that methane hydrates have begun to decompose at all the coasts of Siberia, Canada, in the Greenland sea (see Figure 4), as well as in the tropics of the Atlantic Ocean, near to the western coast of South America and at the coast of Antarctica and in the northern Indian ocean (see Figure 5, 6).

The carried out experiments with a long time of integration have shown, that rather a short-term perturbation of temperature of the ocean surface of the century scale for a long period of time, say, about 5000 years, can result in the saturation of waters of the World ocean by the dissolved methane. The results of the experiments as a whole give a reasonable coincidence of the methane flux estimations from the hydrate decomposition into the atmosphere, i.e., no more than 1 % per year of the annual methane emission from all the sources, with available estimations, [3].

References

[1] Khalil M.A.K., Rasmussen R.A. Sources, sinks and seasonal cycles of atmospheric methane // J. Geophys. Res. — 1983. — Vol. 88 (C9). — P. 5131–5144.

[2] Neue H. Methane emission from rice fields: Wetland rice fields may make a major contribution to global warming // BioScience. — 1993. — Vol. 43 (7), P. 466–473.

[3] Kvenvolden K.A. Gas hydrates — geological perspective and global change // Reviews of Geophysics. — 1993. — No. 31. — P. 173–187.

[4] Kvenvolden K.A. Potential effects of gas hydrate on human welfare // Proc. Nat. Acad. Sci. USA. — 1999. — Vol. 96. — P. 3420–3426.

[5] Scherbakov A.V., Malakhova V.V. Mathematical simulation of the methane inflow into the atmosphere from the ocean methane-hydrates // Bull. Novosibirsk Comp. Center. Ser. Num. Model. in Atm., Ocean, etc. — Novosibirsk, 2000. — Iss. 5. — P. 63–68.

[6] Scherbakov A.V., Malakhova V.V. Mathematical simulation of methane inflow into the atmosphere from decomposed subbottom methane-hydrates // Bull. Novosibirsk Comp. Center. Ser. Num. Model. in Atm., Ocean, etc. — Novosibirsk, 1998. — Iss. 3. — P. 77–82.

[7] Scherbakov A.V., Malakhova V.V. On possible increase of the methane flux into the atmosphere from the destabilized methane-hydrates under changes of the ocean surface temperature // Bull. Novosibirsk Comp. Center. Ser. Num. Model. in Atm., Ocean, etc. — Novosibirsk, 2002. — Iss. 8. — P. 51–58.

[8] Hatzikiriakos S.G., Englezos P., The relationship between global warming and methane gas hydrates in the earth // Chemical Engineering Science. — 1993. — Vol. 48, No.. 23. — P. 3963–3969.

[9] Scherbakov A.V., Malakhova V.V., Antsis E.N. Numerical model of the World ocean with the Arctic Ocean taken into account. — Novosibirsk, 1977. — (Preprint / RAN. Sib. Branch. Inst. of Num. Math. and Math. Geoph.; 1106).

[10] Scherbakov A.V., Malakhova V.V. On the deep water formation in the World Ocean model // Bull. Novosibirsk Comp. Center. Ser. Num. Model. in Atm., Ocean, etc. — Novosibirsk, 2000. — Iss. 6. — P. 73–78.

[11] Mienert J., Andreassen K. Changes of the Hydrate Stability zone of the Norwegian margin from gracial to interglacial times // Annals of the New York Academy of Science / Gas Hydrates challenges for the future. — 2000. — Vol. 912. — P. 200–210.

[12] Buffett B. Archer D. Global inventory of methane clathrate sensitivity to changes in the deep ocean // Earth and Planetary Science Letters. — 2004. — No. 227. — P. 185–199.

[13] Gornitz V., Fung I. Potential distribution of methane hydrates in the worlds oceans // Global Biogeochem. Cycles. — 1994. — No. 8. — P. 335–347.

[14] Hyndman R.D., Davis E.E. A mechanism for the formation of methane hydrate and seafloor bottom-simulating reflectors by vertical fluid expulsion // J. Geophys. Res. — 1992. — Vol. 97. — P. 7025–7041.

[15] Harvey L.D.D, Huang Z. Evaluation of the potential impact of methane clathrate destabilization on future global warming expulsion // J. Geophys. Res. — 1995. — Vol. 100, No. D2. — P. 2905–2926.

[16] Scherbakov A.V., Malakhova V.V. Simulation of the Global ocean response to warming and cooling the surface waters at century scale // Bull. Novosibirsk Comp. Center. Ser. Num. Model. in Atm. Ocean, etc. — Novosibirsk, 2001. — Iss. 7. — P. 69–76.

[17] Kotliakov V.M. The chink at the East station tells about the last climate of the Earth // Program "Global changes of the natural environment and a climate". — Moscow, 1997. — P. 281–291.

[18] Obzhirov A., Suess E., Salyuk A. et al. Methane flares of the Ohkotsk sea // Abstract Book of VI-th International Conference on Gas in Marine Sediments. — 2000. — P. 104.

[19] Linke P., Suess E., Torres M. et al. In situ measurement of fluid flow from cold seeps at active continental margins // Deep-Sea Res. — 1994. — Vol. 41. — P. 721–739.