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Groundwater Modeling of Mercury Pollution at a Former Mercury Cell Chloralkali Facility in Pavlodar City, Kazakhstan

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ABSTRACT: In northern Kazakhstan, there is a serious case of mercury pollution near the city of Pavlodar from an old mercury cell chloralkali plant. The soil, sediment, and water are severely contaminated with mercury and mercury compounds as a result of the industrial activity of this chemical plant. Several international organizations such as the EPA and the EU countries have provided technical and financial support to the Kazakhstan government to remedy this mercury problem. Many mercury study efforts have been done. The aim of this particular project has been groundwater mercury pollution distribution aureole forecasting. This paper provides methods and results of mathematical simulations of hydrogeological conditions in the northern industrial zone of the Pavlodar City chemical plant.

INTRODUCTION

Mercury is an extremely toxic substance, capable of producing irreparable damage to the environment. As a rule, mercury cell chloralkali plants require a great deal of water and are located near water sources. It goes without saying that such a geographical position creates serious danger for these water sources.

Mathematical modeling is the most effective method of investigation of groundwater mercury pollution processes. There was created in Kazakhstan the system of heteroscaled interconnected mathematical models of hydrogeological conditions for the northern part of Pavlodar industrial region. The result of this modeling is to manage and forecast mercury pollution aureole transport direction, to estimate groundwaters pollution dangers for the environment and to develop measures for environmental risk optimization.

Site Description. The territory investigated is situated at the boundaries of Pavlodar region and the Pavlodar district in Kazakhstan. On the site, chemical, oil-processing, carton-ruberoid plants, and power-and-electric stations are operating. On the western part of the region described is situated the village Pavlodarskoe, the inhabitants of which use groundwaters for drinking.

The region is situated on the right shore of the River Irtysh. On the territory investigated the aquifer in modern alluvial depositions of the Irtysh river flood plain (aQ_{IV}), aquifer of Upper-Quaternary depositions of the first supra flood plain terrace (aQ_{III}) and the aquiferous complex in Upper-Miocene Lower-Middle-Pliocene depositions of Pavlodar suite ($N_{1-2}pv$) are distributed. As the first from land surface regional aquiclude are clays of Kalkaman suit of Neogene. Water-holding rocks are presented by sands with interlayers of non-persistent in strike clays, sandy loams, loams. Groundwaters of modern Upper-Quaternary depositions and depositions of Pavlodar suite have a good hydraulic linkage among themselves (Figure 1).

The regional groundwater formations have been formed presumably at the expense of atmospheric precipitation infiltration and inflow from outer boundaries. Groundwaters flow, forming at the depositions of Pavlodar suite, was partly discharging into Upper-Quaternary depositions, and then into the flood plain which was draining into the Irtysh River. Also groundwater discharge has taken place into lake basins, by the way of evaporation and outflow through outer boundaries (Veselov et al., 2002), (Tanton et al., 2004).

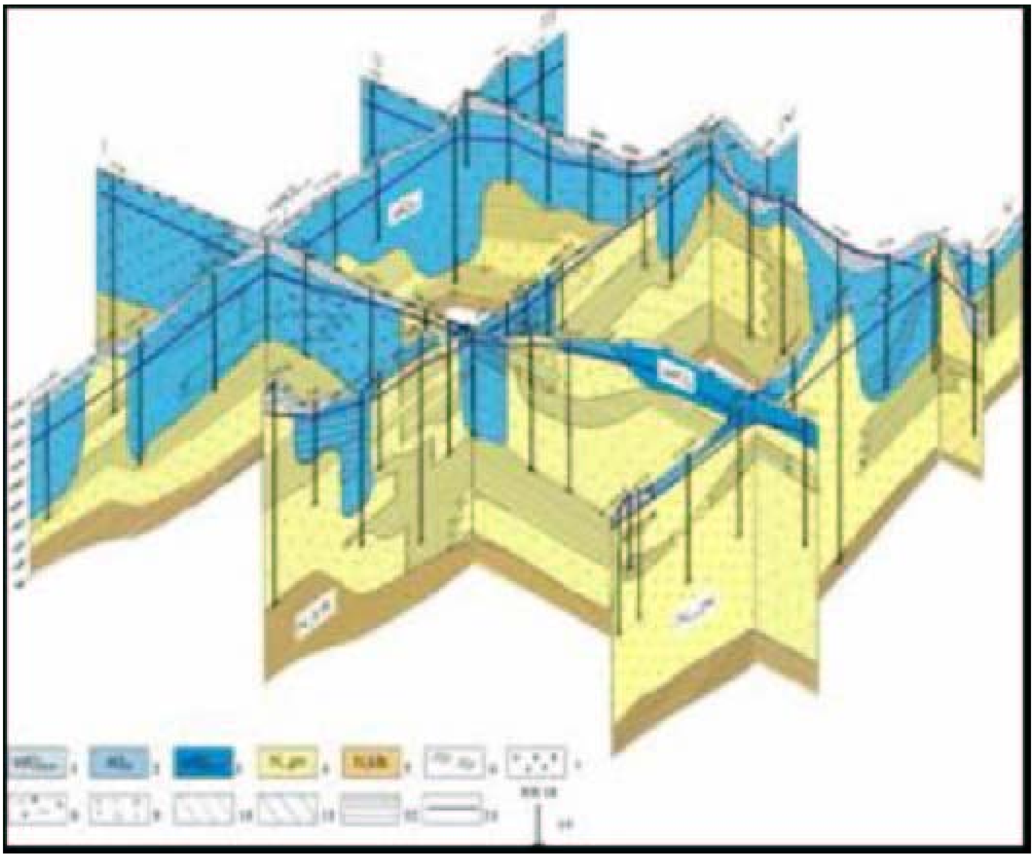

FIGURE 1. Three-dimensional diagram of lithological structure of the region modeled

A considerable influence onto hydrogeological conditions of the region investigated have made technogenic factors—construction of the plants (chemical, oil-processing, et al.), waste waters accumulators—Bylkyldak, Sarymsak, special experimental-industrial storage ponds-evaporators, ash damps from heat and electric power stations, magistral irrigation channel, and irrigation massives, etc.

Pavlodar chemical plant, situated at the distance of 5 km from Irtysh river bed, is the source of the groundwater mercury pollution. The plant has been in operation from 1975 until 1993. Groundwater mercury pollution has been taken place as a result of mercury losses at the mercury cell chloralkali plant (Building 31), and also because of leakage from a pump station which pumped the wastewater from the former mercury cell chloralkali plant. The groundwater flows through an ash dump region and then travels under Building 31 where it picks up mercury contamination and transports it in a northern-western direction.

Preliminary data indicates that the losses of mercury from 1975–1990 were more than 1000 tons and most of the mercury is situated under Building 31 (Tanton et al., 2003; (Ullrich et al., 2004; (Panichkin et al., 2007). Mercury concentration in the groundwater near Building 31 has reached 12.5-103 mg/cubic decimeter. Maximum permissible concentration of mercury in the groundwater is 0.0005 mg/cubic decimeter. The pollution is distributed to a depth of 20 meters (Panichkin, 2007).

MATERIALS AND METHODS

The system of hetero-scaled interconnected mathematical models has been developed with the aim of groundwater mercury pollution aureole distribution forecasting for the prediction of mercury risk into the Irtysh River and wells and pits of the village Pavlodarskoe. The system includes regional and local models (Figure 2).

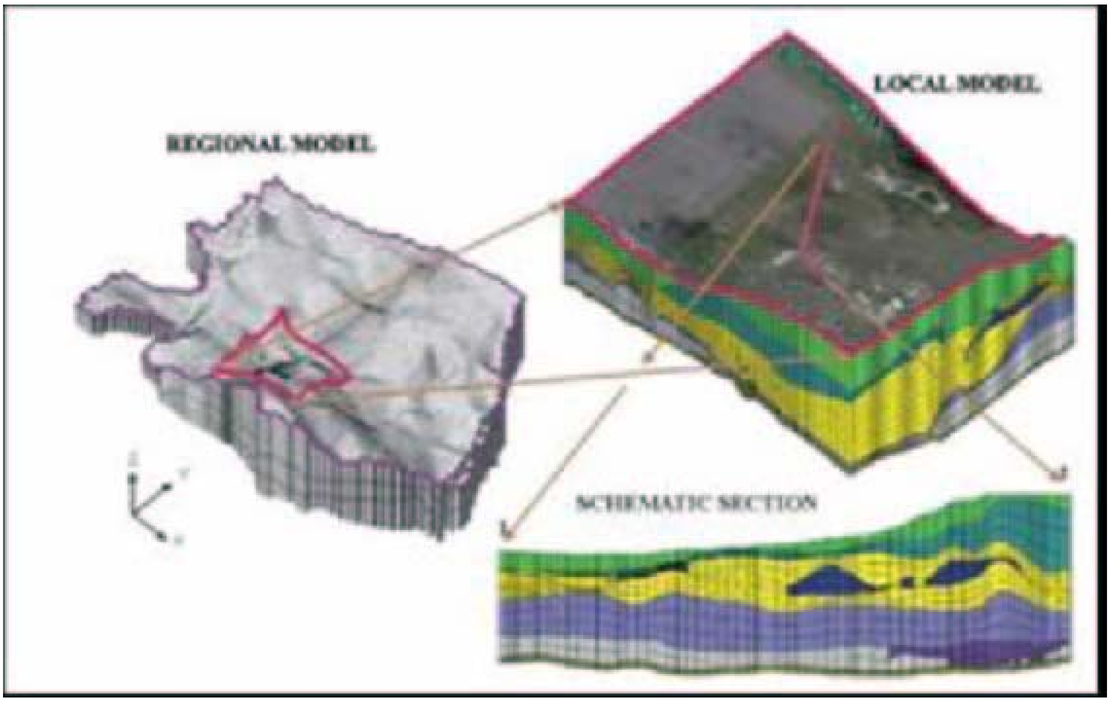

FIGURE 2. Hydrogeological conditions models system structure for the northern part of Pavlodar industrial region

Regional Model. The regional model is intended for groundwaters head level surface position change forecasting, and also for the approximate estimate of change of direction and sizes of mercury pollution aureole. As boundaries of the regional model in plane on west is the Irtysh River, on north—magistral irrigation channel. On east the boundary goes through the chain of lakes. On the model they are schematized by the boundary conditions of the first order. Southernwestern and southern-eastern boundaries of the model are traced by the current streamlets and schematized as impermeable. The lakes Bylkyldak, Sarymsak, and Karabidaik are schematized as inner boundaries of the first order. Groundwater discharge in the result of evaporation is imitated by the boundary conditions of the third order. The region modeled in plane is approximated by rectangular inequalities net, the step of which is changing from 50 to 250 m. Minimal step chosen in this region of groundwaters mercury pollution source—the mercury cell chloralkali chemical plant, maximal one—by the periphery. The region modeled in section was represented in the form of five layers with taking into consideration of the peculiarities of its lithological structure. The model takes in consideration the basic regional factors, producing a considerable influence onto the process modeled—imitates groundwaters charging at the expense of infiltration of atmospheric precipitation, waste waters at the region of the ash dump, reproduces charging of the accumulators Bylkyldak and Sarymsak, water losses from communications. Regional model was developed in the years of 2003–2005 with the help of the software system GMS 3.1 (Panichkin, 2003).

It is worth noting that the regional model didn't take into consideration mercury sorption processes by water-containing rocks. Besides this, too rough schematization of the region modeled in section has not allowed with enough degree of precision to reproduce groundwaters mercury pollution transport in vertical direction. Therefore it has been decided to develop the local model using the updated software program GMS 6.0 (Panichkin et al., 2007).

Local Model. The territory modeled includes the region polluted by mercury and more precisely reflects the change of hydrogeological conditions in space and time (Panichkin et al., 2007). Modeling region in plane is approximated by proportional orthogonal net with the step of 40 m. Hydrogeological conditions in section are schematized in the form of 19 layers. The local model imitates mercury sorption processes by water-containing rocks. It has been used the supposition that equilibrium among soluble and sorbed phases of mercury establishes momentarily and sorption is irreversible. Therefore, for its description we have used the linear isotherm of Henry:

$$\check{C} = K_d C \ ,$$

where $\check{C}$ [MM^{-1}] – sorbed concentration, C [M/L^3] – dissolved concentration, K_d [L^3M^{-1}] – distribution coefficient.

Sorption constant values for sandy and clayish rocks were given from the results of laboratory determinations. Distribution coefficient changes in the boundaries from 0.01 to 0.04 decimetre3/mg for clayish rocks, and from 0.00001 decimetre3/mg for inequigranular sands to 0.0015 decimetre3/mg for clayish and dusty ones. Porosity for clayish rocks was 0.3, for sandy rocks – 0.22. Mercury concentration in the sources was changing from 0.3 to 0.04 [mg/decimetre3].

Now on the territory of Pavlodar industrial region are already constructed filtration screen around the basic sources of groundwater pollution. They are imitated on the local model as aquifer absence regions.

Interrelation of local and regional models has been made by the way of assigning of the heads as of the boundary of local model. They are calculated by interpolation of hydrodynamic task solution results on the regional model into limiting blocks of the local model (Figure 3).

Calibration of the local model is executed after its formation. Its quality has been estimated as of the degree of its conformity with the existing natural conditions, with taking into consideration of the results, produced on the regional model. The calibration has included into itself the solution of the series of inverse tasks: stationary and transient hydrodynamic tasks, the task of mercury transport by the groundwater flow.

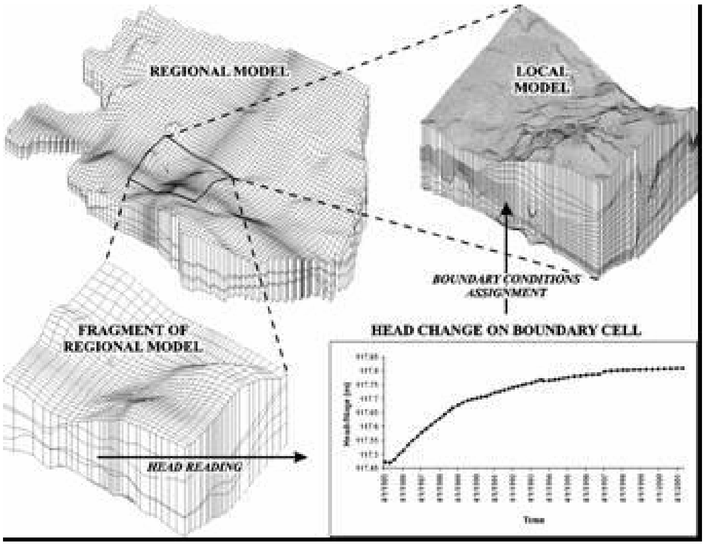

FIGURE 3. Assigning of absolute marks of the head as of outer boundaries of the local model.

During solution of the inverse stationary hydrodynamic task, position of groundwater heads was reproduced onto conditionally undisturbed period (1970). Surface head level change from 1970 until 2007 was imitated by the solution on the model of the inverse transient hydrodynamic task. Specific yield coefficient was assigned as equal to 0.22. Specific storage of the water-containing rocks was equal to 0.001 [1/m]. Maximal value of groundwaters recharge at the expense of the losses from engineering communications reached 0.002 [m/d]. Inverse task of transport (1975–2007) has been solving for the mercury transport process modeling by the groundwater flow in plane and in section. Advective component of substance flow was calculated coming from hydrodynamic task solution.

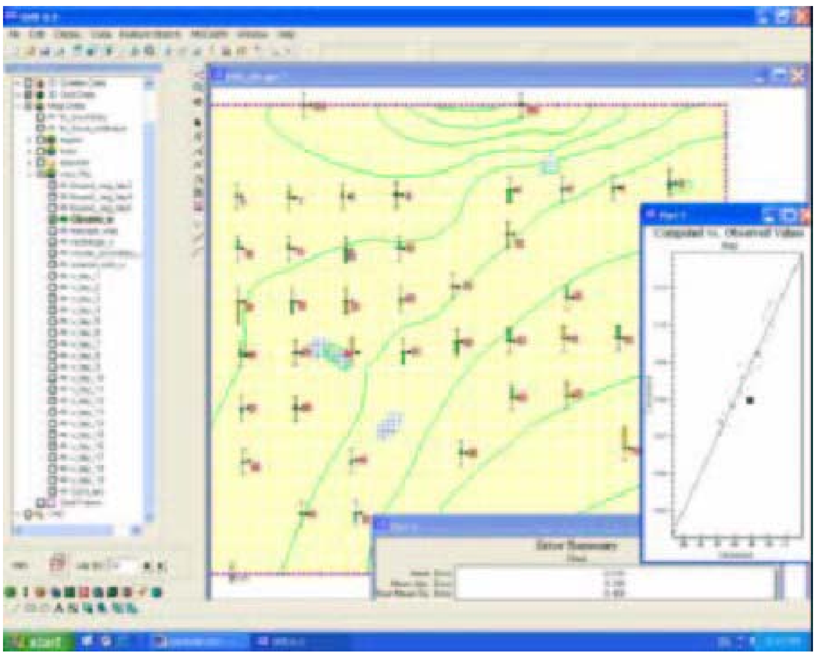

FIGURE 4. Inverse stationary task solution result.

Coincidence, with reasonable degree of precision, of calculated values of heads and concentrations with values, received at the result of execution of the field and laboratory investigations allows to speak about adequacy of improved local model with the existing natural conditions (Figures 4 and 5).

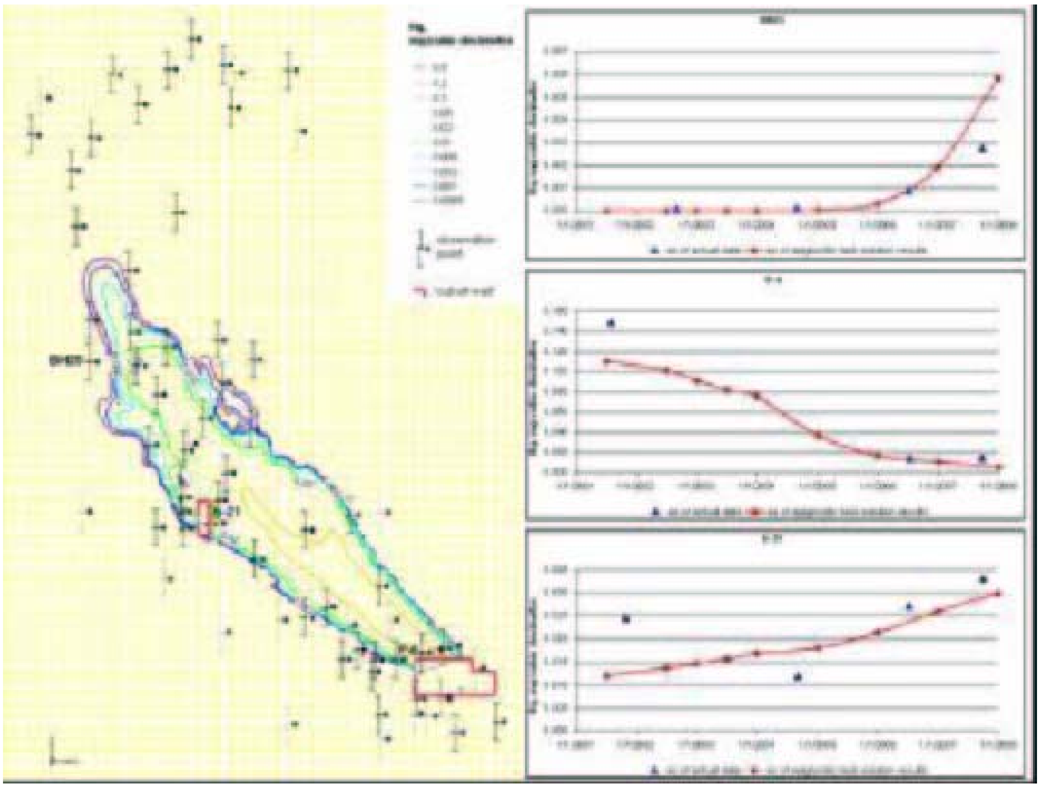

FIGURE 5. Result of the solution of the inverse task of transport.

RESULTS AND DISCUSSION

The regional model has taken into consideration the basic factors, producing considerable influence onto the process modeled. It has been used for the rough forecasting of groundwaters mercury pollution aureole distribution direction. It has been made on it four variants of prognosis for the period of 30 years. The first variant presupposed conservation of the existing sources of pollution (under department and at the region of pump station, realized earlier the transport of mercury-containing industrial wastes into accumulator Bylkyldak). The second one—localization of sources under the department, as it has been presupposed by the program as of demercurization of the chemical plant territory. At the boundaries of the third variant has been imitation the elimination of water losses at the region of sewage purification equipment, at the result of which was groundwater flow direction change and, as a consequence—pollution aureole transport direction. Localization of the two basic sources of pollution, situated under the department and in the region of pump station, with the help of the filtration curtain of the type "cut-off-wall," has been reproduced during execution of the fourth variant of prognosis.

Solution of the forecasting tasks of the regional model allows speaking about mercury occurrence danger absence during the nearest decades into Irtysh River and into wells and pits of the village Pavlodarskoe under conservation of the existing hydrogeological conditions. In accordance of the results of the forecasting, isolation of the basic mercury sources will stop further local pollution of groundwaters.

The results of the solution of the forecasting tasks on the regional model have been taken into consideration during planning of demercurization measures. Solution has been adopted about construction of the filtrational curtains of the type “cut-off-wall” around Building 31 and the pump station, produced earlier the transport of mercury-containing wastes. These measures were made during the years of 2003–2004.

For the estimation of the effectiveness of the measures adopted, the local model has been developed which more precisely takes into consideration lithological structure of the hydrogeological object and the processes of mercury sorption by water-containing rocks. Transport of solutes in groundwaters mercury not only in horizontal but also in the vertical direction has been reproduced on the more precise local model. Task of prognosis of mercury transport by the flow of the groundwaters has been soluting for the period of 30 years (2007–2037). It was possible, as of the results of the solution, to conclude that to the end of prognosticated period groundwaters mercury pollution aureole will be preserved, though the great quantity of mercury will be sorbed by clayish rocks (Figure 6). In the result of groundwaters evaporation from the head level surface, the mercury pollution aureole will rise upstairs through “windows” in clayish layers and mercury consideration in water near groundwaters table will increase. This will give a definite danger of mercury occurrence from groundwaters into soil and accumulation of it in vegetation.

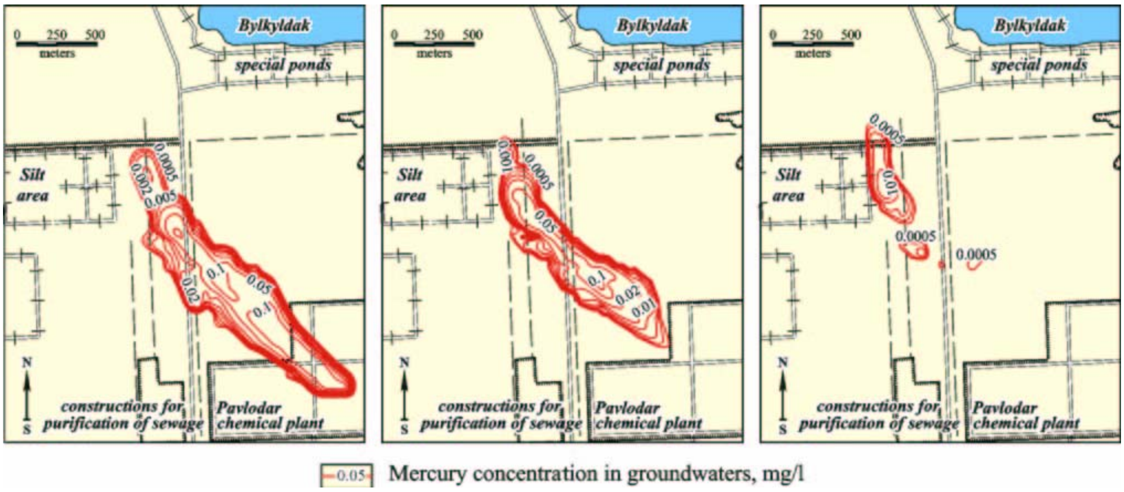

FIGURE 6. Result of the solution of the task of prognosis.

CONCLUSIONS

Utilization of the system of hetero-scaled interconnected mathematical models is a very effective technique during investigation of the territories, subjected to the technogenic pollution of groundwaters. The regional model is used for the producing of preliminary forecasts, the local one—for its more precise determination. This allows more safely to estimate risks and to give more precise recommendations for its minimization.

Now on the territory investigated anthropogenic impact in considerable degree determines hydrogeological conditions. Therefore organization of monitoring and establishment of constantly acting systems of models is a perspective direction of further investigations. It will allow more operatively tracing the changes of hydrogeological conditions, to forecast further distribution of groundwaters mercury pollution aureole, and to estimate effective measures conducted for demercurization.

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