MATHEMATICAL MODELING OF GROUNDWATER MERCURY POLLUTION (CASE OF NORTHERN INDUSTRIAL AREA OF PAVLODAR CITY, KAZAKHSTAN) Vladimir Yu. Panichkin¹, Oxana L. Miroshnichenko¹, Mikhail A. Ilyushchenko², Trevor

W.Tanton³, Paul M. Randall⁴

¹ Institute of Hydrogeology and Hydrophysics, Almaty, Kazakhstan, <u>v_panichkin@mail.kz</u>
² Almaty Institute of Power Engineering and Telecommunication, Kazahkstan, <u>mai2@mail.ru</u>
³ University of Southampton, Southampton, UK, <u>T.W.Tanton@soton.ac.uk</u>
⁴ U.S. EPA, Cincinnati, Ohio USA, <u>Randall.paul@epa.gov</u>

In northern Kazakhstan, there is a serious case of mercury pollution near the city of Pavlodar from an old mercury cell chlor-alkali plant. The soil, sediment, and water is 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/poster provides methods and results of mathematical simulations of hydrogeological conditions in the northern industrial zone of the Pavlodar City chemical plant.

INTRODUCTION

Mathematical modeling is the most effective method of investigation of groundwater mercury pollution processes. There was created in Kazakhstan the system of hetero-scaled interconnected mathematical models of hydrogeological conditions for the northern part of Pavlodar industrial region. In the result of modeling it managed to forecast mercury pollution aureole transport direction, to estimate groundwaters pollution dangers for the environment and to develop measures for risk lowering.

Administratively, the territory investigated is situated at the boundaries of Pavlodar region, Pavlodar district (Republic of Kazakhstan). Immediately on the working site chemical, oil-processing carton-ruberoid plants, power-and-electric stations are functioning. On the western part of the region described is situated the village Pavlodarskoe, the inhabitants of which use groundwaters for drinking.

The region in question 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 (Fig. 1). 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 (Fig. 2).

Regional groundwater formation in natural conditions has been made 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 flood plain which was draining by the Irtysh river. Also groundwaters discharge has taken place into lake basins, by the way of evaporation and outflow through outer boundaries (4, 7).

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 et al.



1 – regional model boundary, 2 – local model boundary, 3 – hydrogeological well and its number, 4 – line of hydrogeological section and its number

FIGURE 1. Site of the region investigated



1 - water-permeable practically nonaqueous Upper-Quaternary and Modern depositions; 2 – aquifer in Upper-Quaternary Alluvial depositions; 3 – sporadically flooded Middle-Quaternary Alluvial- Deluvial depositions; 4 – Aquiferous complex in Lower-Middle-Pliocenic, Upper-Miocenic depositions of Pavlodar suite; 5 – Water-resistant rocks in Lower-Middle- Miocenic depositions of Kalkaman suite; Lithological composition of rocks: 6 – soil; 7 – sand; 8 - clayish sand; 9 – gravelly sand; 10 – sandy loam; 11 – loam; 12 – clay; 13 – head surface of groundwaters; 14 – hydrogeological well and its number.

FIGURE 2. Three-dimensional diagram of lithological structure of the region modeled

Pavlodar chemical plant, situated at the distance of 5 km from Irtysh river bed, is the source of groundwaters mercury pollution. It has been at exploitation from 1975 till 1993. Groundwater pollution has been taken place mostly in the result of mercury losses at the caustic soda production department (department No 31), and also because of leakage from communication at the region of pump station, doing the pumping of mercury-containing industrial waters. Groundwaters flow, forming at the ash dump region, goes under the caustic soda production department, is polluted by mercury and transport it in northern-western direction.

In accordance with the data of preliminary observations, losses of mercury at the period of 1975 - 1990 were more than 1000 tons, and this case the greater part (about 1000 tons) proved to be situated under department No 31 (2, 3, 5, 6). Mercury concentration at groundwaters near the department No 31, has reached the value of 12.5-103 mg/cubic decimeter. Maximal admissible concentration of mercury at groundwaters is 0.0005 mg/cubic decimeter. The pollution was distributed to the depth of 20 meters.

MATERIALS AND METHODS

The system of hetero-scaled interconnected mathematical models has been developed with the aim of groundwaters mercury pollution aureole distribution forecast for the estimation of mercury occurrence danger into Irtysh river and wells and pits of the village Pavlodarskoe, and also for the development of measures for risk lowering. The system includes regional and local models (Fig. 1, 3).



FIGURE 3. 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. 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 regione of 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 system GMS 3.1 (1).

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 on the base of the programming complex GMS 6.0 (2, 3).

Local model. The territory modeled includes the region polluted by mercury and more precise reflects the change of hydrogeological conditions in space and time (Panichkin et al., 2007). 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:

$$C = K_d C$$
,

where \overline{C} [MM⁻¹] – sorbed concentration, C [M/L³] – dissolved concentration, K_d [L³M⁻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.

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.

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 till 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.

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 (Fig. 4 and 5).



FIGURE 4. Inverse stationary task solution result



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 to speak 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 has 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 the department No 31 and 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 effectivity 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 soluted 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 (Fig. 6). In the result of 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 the further investigations. It will allow more operatively to trace the changes of hydrogeological conditions, to forecast further distribution of groundwaters mercury pollution aureole, to estimate effective measures conducted for demercurization.

ACKNOWLEDGMENTS

Funding of this study was provided by the INCO-Copernicus under Grant No. ICA2-CT-2000-10029 "Development of cost-effective methods for minimising risk from heavy metal pollution in industrial cities: A case study of mercury pollution in Pavlodar", and by the ISTC under Grant No. K-1240 "Post-containment Management and Monitoring of Mercury Pollution in Site of Former PO "Khimprom" and Assessment of Environmental Risk Posed by Contamination of Groundwater and Adjacent Water Bodies of the Northern".

REFERENCES

- 1. Panichkin V.Yu. 2003. "Methods, technology and results of groundwaters mercury pollution, modeling of Pavlodar industrial region". *Proceeding of National Academy of Sciences, Series of geology, No 5*, pp. 72-78.
- 2. Panichkin V.Yu. 2007. "Risk assessment from groundwater mercury pollution of the Northern area of Pavlodar industrial region by the methods of mathematical modeling". *Report on the International Workshop "Environmental mercury pollution: mercury emissions, remediation and health effects"*, Department of Environmental protection, Astana, Kazakhstan.
- 3. Panichkin V.Yu., Miroshnichenko O.L., Vinnikova T.N., Trushel L.Yu., Zakharova N.M. 2007. "Groundwaters mercury pollution process investigation of Pavlodar industrial region (Kazakhstan) by the methods of the mathematical modeling". *Report on the International symposium "The future of hydrogeology: modern tendencies and perspectives"*, St. Petersburg State University, St. Petersburg, Russia.

- 4. Tanton T.W., Ullrich S.M., Daukeev G.Zh., Ilyushchenko M.A., Lapshin E.V., Veselov V.V., Panichkin V.Yu., Kamberov I.M.. 2004. "Results of investigation of mercury contamination in Northern industrial area of Pavlodar; proposals for the demercurization of this territory". *Proceeding of III International scientific conference "Heavy metals, radionuclides and elements-biofils in the environment (Semipalatinsk, 7-9 October 2004)"*. Semipalatinsk state pedagogical institute, Semipalatinsk, Kazakhstan. V.1, pp. 72-77.
- 5. Tanton T.W., Veselov V.V., Ilyushchenko M.A., Panichkin V.Yu. 2003. "Risk assessment from mercury contamination of Northern industrial site of Pavlodar city". *Reports of National Academy of Sciences of the Republic of Kazakhstan*. No 4, pp.78-81.
- Ullrich S.M., Ilyushchenko M.A., Panichkin V.Y., Kamberov I.M., Tanton T.W. 2004. "Mercury pollution around a chlor-alkali plant in Pavlodar, Northern Kazakhstan. RMZ-Materials and Geoenvironment". *Special issue: Mercury as a Global Pollutant*, V. 51, No 1, pp. 298-302.
- 7. Veselov V.V., Panichkin V.Yu., Lushin E.N. 2002. "Groundwaters mercury pollution investigation at the northern part of Pavlodar industrial region". *Report on International scientific-practical conference "Natural-humanitarian sciences and their role in engineering cadres education*". Kazakh National Technical University, Almaty, Kazakhstan.