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Monitoring the Effectiveness of Measures to Contain the Primary Sources of Mercury Pollution on the Site of a Former Chloralkali Plant in Kazakhstan

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ABSTRACT: An extensive sampling campaign was conducted in 2005–2007 to monitor the effectiveness of remedial measures to contain mercury pollution at the site of a former mercury cell chloralkali plant in Pavlodar, Kazakhstan. Containment measures consisted of cutoff walls and capping of the primary mercury sources. There are concerns in the northern boundary of the Pavlodar Chemical Plant of possible changes of the groundwater plume direction and/or upward movement of mercury-polluted groundwater to the surface in the pastures of the depression next to Lake Balkyldak; high levels of mercury contamination in Lake Balkyldak, as well as the fish within it; and high levels of mercury-contamination in waste lagoons near the lake. Initial results show that where there was a high hydraulic gradient in the soil (i.e., at the waste lagoons adjacent to Lake Balkyaldak), there is an observable beneficial effect from installing of a cut off wall and capping of the waste lagoons with the source of pollution being contained. The beneficial effects of isolating and capping the large primary source of mercury pollution below the former mercury cell chloralkali factory site can not so easily be observed. The mercury plume from the factory site appears to be advancing as modeled, with Hg arriving at the next two bore holes in the path of the plume. However, during a three-year monitoring program there were quite high systematic changes in mercury concentration in many of the wells that cannot be readily explained by the hydraulic properties of the soil or the groundwater pollution models. It is considered that these changes are most likely the result of fluctuations in groundwater levels during the study period influencing borehole "effective" sampling zone within the plume. This makes long-term monitoring of changes in soil water mercury concentration and plume dispersion difficult.

INTRODUCTION

Mercury pollution in Pavlodar, Kazakhstan resulted from mercury cell chloralkali production activity from 1975–1993. Typical production capacity was approximately 100,000 tons of chlorine per year. Since then, the revenues from plant operations have declined drastically, and the plant is currently in financial and physical disrepair. The intentions of the current plant management is to equip the plant with new chlorine production lines using membrane technology, however, it has not been implemented due to lack of funding.

For many years, the U.S. and the European Union have provided technical and financial support to Kazakhstan to engage many engineers and scientists in cooperative research environmental projects as well as several mercury projects. The U.S. projects are implemented through the International Science and Technology Center (ISTC), an intergovernmental organization dedicated to the nonproliferation of weapons and technologies of mass destruction. ISTC pursues this objective by funding peaceful scientific and technical research to former weapons scientists in Russia and the Commonwealth of Independent States countries, using their skills for nonweapons development projects. The U.S. State Department is attempting to engage personnel at the Pavlodar Chemical Plant in commercially sustainable activities.

FIGURE 1. Former mercury cell chloralkali plant, Building 31.

Research studies carried out at the Pavlodar Chemical Plant have provided evidence of extensive mercury pollution. One study by a Kiev scientific organization concluded that there was approximately 1300 tons of metallic mercury deposited underneath the mercury cell production building (i.e., Building 31). Another study funded by the European Union reported that the area of topsoil contamination is much higher than was expected as well as mercury contamination in waste ponds nearby and in the sediments in Lake Balkyldak. Furthermore, the mercury-contaminated groundwater plume (about 400 m wide with $HgCl_2$ up to a concentration level of 0.1 mg/L) has spread over the basalt clay stratum at the depth of 5–20 m and was moving from the mercury cell Building 31 NNW as a result of the hundreds of tons of metallic mercury under the building. Furthermore, an additional mercury hotspot was located at the wastewater pump station No. 6. This data significantly increased the scope of activities required for containment of the primary mercury sources and risk management.

In 1998, enough funding became available for the roof removal of Building 31, which led to extensive mercury vaporization in the spring of 1999. The city of Pavlodar declared a state of emergency. Under the pressure of public and mass media, the Kazakhstan government allocated the funds for both dismantling the contaminated part of Building 31 and mercury separation and collection. After the funding was spent, the remediation effort was halted.

In 2002, further funding was obtained from the Kazakhstan government to continue remedial activities at the site. Dismantling of Building 31 and the disposal of construction waste with a mercury content <1.0 % by wt in a landfill located 70 m south of Building 31. The landfill was designed to be a pit that contained a low permeable clay barrier (1 x 10-7 cm/ sec). The landfill was capped with asphalt. To prevent spreading of residual mercury in groundwater from beneath Building 31, a bentonite cutoff wall (15–20 m deep, 0.5 m wide) was constructed to isolate this area (Figure 2). Furthermore, a cutoff wall was constructed around the waste lagoons near Lake Balkyldak and pump station No. 6.

The cutoff wall was constructed by backfilling a trench with a mixture of bentonite clay and water which was deep enough to reach water-resistant basalt clay under the aquifer. In addition, in the area outside the cutoff wall, the upper layer of soils contaminated with mercury over 10 mg/kg was removed to a depth of 50 cm and placed inside the cutoff wall perimeter. Excavated soil was replaced with clean soil. These remedial measures were completed in 2005.

FIGURE 2. Construction of the bentonite cutoff wall.

POST-DEMERCURIZATION MONITORING RESULTS

Post-demercurization monitoring was conducted in 2005–2007. Measurements of total mercury content in water samples taken from observation boreholes network showed that the level of dissolved mercury concentration were the same during the three years of monitoring. Significant local decrease in mercury concentration in the groundwater was observed only at the territory of the chemical plant outside of the site of chloralkali production factory. The possible reason for this could be slight deviation of the plume of contamination under flank action of new sources of water loss from underground sewage system of the plant rather than cessation of the groundwater recharge with soluble mercury compounds from the main underground hotspot. It was shown that topsoil contamination with metallic mercury at the former chloralkali factory site was still abnormally high (up to 0.1% mass) and was a source of emission of high mercury concentration vapors to atmosphere (above the level of 300 ng/m3 in near-earth air layer 0.5 m thick at 27°C). The same topsoil could become the main source of groundwater recharge with soluble mercury compounds due to infiltration of atmospheric precipitation and flood flows through it that in general kept high level of mercury concentrations in the groundwater within the industrial site. The plume of contamination also kept a tendency to transition of dissolved mercury of high concentrations in the direction of groundwater movement resulted in finding mercury in earlier uncontaminated observation boreholes of the monitoring network which monitored west direction of the mercury spread.

Soil sampling outside of the industrial area of the chemical plant allowed finding one more mercury hotspot at the area of a pasture inhabitants of nearby village used for their livestock. A level of the topsoil contamination was 100 mg/kg; the area of contaminated site was not less than 0.05 km2; the place of contamination coincided with the area of the plum of groundwater mercury contamination spread at the depth of 6–8 m.

A regional hydro-geological model of the Northern industrial area of Pavlodar was produced with help of a system of computer simulation GMS 3.1, database formed on the basis of data collected on the special monitoring network from more than 100 observation boreholes for two years as well as historical data on the industrial area including description of more than 2000 boreholes constructed here for 40 years. In 2007 the model was converted to GMS 6.0 software format and improved by a local model of the groundwater mercury contaminated area as well as data of monitoring of 2004–2006. The regional model allowed explaining mechanism of formation of the plume of groundwater mercury contamination, gave possible scenarios of its development and predicted groundwater rise up to the ground surface at some places and topsoil mercury contamination caused by the groundwater evaporation. It was shown that even at complete cessation of groundwater recharge from both underground hotspots and topsoil, the mercury contamination would still exist in the groundwater plume for more than thirty(30) years slowly shrinking and bringing mercury concentration levels down due to dilution and sorption processes. However, the dynamics of the groundwater plume is not well understood and there are many factors that may cause a directional change as well as changes in the groundwater mercury concentration levels.

Monitoring of seasonal variations of water-level of the waste lagoons continues. Underground recharge of the waste lagoons is provided by a joint ash lagoon (located 5 km to the south) near the two coal-fired power plants. In Lake Balkyldak, about 2.6 km^2 of its shoreline is covered with reed thickets while total water-surface area is 17.8 km^2. Sampling was conducted in the winter from under the ice(approximately 1 m thick) because summer sampling was difficult with rough waters. Technogenic silts were found to be accumulated only in a few depressions resulting in formation of deposits up to 1.75 m thick at the area of 5.9 km2. Mercury concentration in the silts reached 1 g per kg of dry weight and the amount of mercury there was estimated to be about 130 tons. Mercury concentration in fish reached its maximal value of 2.5 mg/kg.

SUMMARY

Post-demercurization monitoring will continue for several more years. Initial results show that where there was a high hydraulic gradient in the soil (i.e., at the waste lagoons adjacent to Lake Balkyaldak), there is an observable beneficial effect from installing of a cut off wall and capping of the waste lagoons with the source of pollution being contained. The beneficial effects of isolating and capping the large primary source of mercury pollution below the former mercury cell chloralkali factory site can not so easily be observed. The mercury plume from the factory site appears to be advancing as modeled, with Hg arriving at the next two bore holes in the path of the plume. However during a 3 year monitoring program there were quite high systematic changes in mercury concentration in many of the wells that cannot be readily explained by the hydraulic properties of the soil or the groundwater pollution models. It is considered that these changes are most likely the result of fluctuations in groundwater levels during the study period influencing borehole “effective” sampling zone within the plume. This makes long term monitoring of changes in soil water mercury concentration and plume dispersion difficult.

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- Mercury pollution at Pavlodar. http://Hg-Pavlodar.narod.ru
- Mercury pollution management in Kazakhstan. http://Hg-Kazakhstan.narod.ru