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## **ANNUAL REPORT**

**for the first year**

**on ISTC K-1240p project**

**“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 Industrial Area of Pavlodar”**

Contracting Institute:

Non-profit JSC “Almaty Institute of Power Engineering and Telecommunications”, BG Chair of Environmental Technology

Participating Institutes:

- 1. Institute of Hydrogeology and Hydrophysics (IHH)**
- 2. JSC “Pavlodar Chemical Plant” (PCP)**
- 3. Pavlodar State University (PSU)**
- 4. JSC “Biomedpreparat – Engineering Center” Laboratory of Monitoring (BMP)**

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## **6. Brief description of the work plan: objective, expected results, technical approach:**

### **6.1. Objectives of the project**

I. to identify the risk associated with the spread of groundwater plumes contaminated with mercury and oil derivatives, including their movement through the network of water intake boreholes in village Pavlodarskoye, and further towards river Irtysh and/or their rise onto the pastures and, if significant, identify a management strategy to contain risk;

II. to identify a management strategy for containing the environmental risk, caused by the mercury pollution of lake Balkyldak, including the pathway of pollutants bioaccumulation via food chains;

### **6.2. Expected results**

The reported study is an applied research in the field of environmental protection. It is assumed that in the course of this work new facts might be revealed that would require the deepening and the extension of the research.

- One of the most important results of proposed study will be the foundation of monitoring laboratory of PCP that will be capable to implement Post-containment monitoring Program in Northern industrial area of Pavlodar during 2005-2020 and to conduct other investigations in the field of environmental protection. The completion of Phase I of Demercurization Project does not assume termination of the investigation of mercury pollution in Pavlodar. The Phases II and III are starting that will require more detailed and more extensive studies of the residual mercury pollution and associated risk. These reasons will allow the laboratory of PCP to become self-supporting;
- PCP together with AIPET will carry out the monitoring study of the mercury contamination of groundwater in the Northern industrial area of Pavlodar;
- AIPET together with PCP will study the extent of mercury contamination of pastures in the areas where the upward movement of polluted groundwater is possible;
- BMP together with PCP will conduct the monitoring study regarding to the groundwater contamination with petroleum and oil products in Northern industrial area of Pavlodar;
- AIPET together with PSU will determine the levels of total mercury content in bottom sediments and biota from wastewater storage pond – lake Balkyldak;
- AIPET together with IHH will assess the risks associated with the residual mercury contamination of groundwater and wastewater storage pond – lake Balkyldak;
- IHH together with AIPET will assess the risks posed by contamination of groundwater with petroleum and oil products;
- IHH will upgrade the groundwater model for the Northern industrial area of Pavlodar and make it more accurate. IHH will make forecasts for the future spread of groundwater contaminated with Hg and oil products;
- AIPET together with IHH will draw up and discuss with local stakeholders and state authorities the proposals for risk management in Northern outskirts of Pavlodar including possible implementation of 2<sup>nd</sup> stage of PO “Khimprom” demercurizing and/or brining wastewater storage pond – lake Balkyldak to safe conditions.

### 6.3. Technical Approach

During sampling and chemical analyses the methods recommended by US EPA will be used as well as standard procedures on Quality Control/Quality Assurance accepted in the West. Determination of mercury in solid samples will be carried out using AAS analyzer (Lumex RA 915+); AFS analyzer (PS Analytical Millennium Merlin System) will be used for Hg determination in water samples and biological tissues. Chemical analysis of oil products' concentration in water will be conducted using CG Perkin Elmer Clarus 500.

Assessment and management of risk associated with groundwater contamination will be carried out using hydrogeological models received by means of the ModFlow GMS 5.0 software. The preliminary assessment of risk (Tier 1 of risk assessment) posed by mercury contamination of pastures and fish will be conducted using the monitoring of the level of mercury pollution and subsequent comparison of pollution indices with existing state standards and guidelines values.

## 8. Technical progress during the first year

### 8.1. Work performed in compliance with tasks and milestones

#### 8.1.1 Study of the movement of mercury in the groundwater rise in depressed area in saturated and unsaturated zones and its accumulation in the shallow ponds and vegetation. Development of management strategy to contain the risk to population in the vicinity and livestock (Task 1)

8.1.1.1 *Groundwater survey*: in June-July of 2006 groundwater samples were taken from 87 hydrogeological observation boreholes for total mercury determination, and also from 2 observation boreholes for methyl mercury determination; twice in July and September of 2006 groundwater tables were measured in 239 observation boreholes.

8.1.1.2. *Plan of soil sampling has been produced* on a regular grid at five places of mercury contaminated groundwater possible wedging out at the territory between the 1<sup>st</sup> industrial area of Pavlodar Chemical Plant and Lake Balkyldak.

8.1.1.3. *Soil sampling*: in July, 2006 19 topsoil (0-10 cm) samples were taken at the industrial area of former chlor-alkali production; in September, 2006 111 topsoil samples were taken on regular grid from 5 places of mercury contaminated groundwater possible wedging out at the territory between the industrial area #1 and wastewater storage pond – Lake Balkyldak for their analyses for total mercury..

8.1.1.4. *Measurement of mercury vapor concentration in the near-earth air (0-10 cm)*: 20 measurements were done at the industrial area of former chlor-alkali production on the 21<sup>st</sup> of July, 2006 since 3 pm till 6 pm at the air temperature of 27° C.

8. 1.1.5. 270 water samples, 140 bottom sediment samples and 27 soil samples have been analyzed for total mercury content and 3 water samples have been analyzed for methyl mercury content.

8.1.1.6. Electronic summary tables (“Summary tables 02 - 07.2006”), which formed the *database of post-demercurization monitoring in site of the industrial area of former JSC “Khimprom”, Pavlodar have been compiled* on the results of field study and chemical analytical works.

8.1.1.7. *The results of determination of mercury concentration in groundwater at the area of mercury pollution (“Summary table 05.2006) have been inserted on the vector map together with the results of similar research of 2004 and 2005.*

**8.1.2. Assessment of possibility for mercury-polluted groundwater flow to change its direction; study of interaction of contaminated groundwater with bearing strata and underlying aquifers (Task 2):**

8.1.2.1. *GMS 6.0 simulation system has been purchased, its characteristics and potential to simulate mercury transport by groundwater have been studied. The regional model of hydrogeological conditions of the Northern industrial area of Pavlodar has been converted into upgraded version of GMS 6.0 software.*

8.1.2.2. *First stage of calibration of the hydrodynamic model of groundwater at the area of former PO “Khimprom” has been completed. Inverse stationary task has been solved. Position of groundwater table as of 1970 i.e. conditionally undisturbed period was reproduced in the model. Filtration coefficients of water bearing strata and a value of groundwater infiltration recharge have been made more precise.*

**8.1.3. Study of the spread of groundwater plume contaminated with oil products from the territory of Pavlodar Oil Refinery; development of model and assessment of environmental risk posed by oil-products contamination of groundwater in the Northern industrial area of Pavlodar (Task 3):**

8.1.3.1. *In the Republican Center of Geological Information “Kazgeoinform”, Kokchetav city additional archival data on groundwater level regime and also information on oil products concentration in groundwater at the Northern industrial area in Pavlodar have been collected.*

8.1.3.2. *4 boreholes 5.5 m deep were drilled with help of a hand drill in the vicinity of western fence wall of industrial area of Pavlodar Oil Refinery and the method of finding distribution border of underground hot spot of oil products pollution has been developed.*

**8.1.4. Assessment of possibility to contain the risk posed by mercury pollution of lake Balkyldak including the fish within it (Task 4)**

8.1.4.1. *The area of the wastewater storage pond – Lake “Balkyldak” in GIS of the Northern industrial area of Pavlodar produced earlier in 2000-2001 has been made more detailed and completed with new data from satellite images and archival documents and also from direct measurement with help of portable GPS: vegetation boundary and the bottom contour of the lake have been input and its nawayday shore line has been made more correct.*

8.1.4.2. *Был составлен План пробоотбора по регулярной сети донных отложений накопителя Балкылдак на 200, 150, 100 и 50 точек отбора, который в зависимости от сложности полевых работ и сроков их выполнения можно было откорректировать на месте.*

8.1.4.3. *Bottom sediments sampling and measurement of soft sediment thickness in wastewater storage pond – Lake Balkyldak: in February, 2006 107 bottom sediment samples were taken from under the ice in 52 sampling points and in July, 2006 33 samples - from the boat board in 17 sampling points.*

8.1.4.5. *The computer map of depths of wastewater storage pond Balkyldak and thicknesses of its bottom sediment has been produced within GIS of Lake Balkyldak using software ArcGIS, module Spatial Analyst.*

8.1.4.6. The results of determination of mercury concentration in bottom sediment samples (“Summary table 08.2006”) have been used to *create preliminary vector map “Mercury contamination of bottom sediments of wastewater storage pond Balkyldak” and preliminary calculation of amount of mercury deposited in the bottom sediments of the pond.*

8.1.4.7. *Biota sampling from wastewater storage pond – Lake Balkyldak and the control water body:* in June-August, 2006 116 silver crucian (including 60 ones for morphological analysis and 56 ones – for chemical analyses), 1 carp (for chemical analyses), molluscs, benthos organisms and plankton organisms – 1, 4 and 2 samples respectively (both for morphological analysis and chemical analysis for total mercury content) were caught.

8.1.4.8. Electronic summary tables (Summary tables 01 and 08.2006), which formed the *database of wastewater storage pond – Lake Balkyldak mercury monitoring* were compiled based on the results of field study at lake Balkyldak and chemical analytical works.

**8.1.5. To draw up and discuss with local stakeholders the recommendations for the 2<sup>nd</sup> stage of demercurization and other remediation activities in the area of the former PO “Khimprom” (Northern industrial area of Pavlodar), including the recommendation for abolishment or further safe use of the wastewater storage pond – lake Balkyldak (Task 5)**

8.1.5.1. The results of the mercury monitoring have been discussed a few times with administration of Pavlodar Territorial Environmental Protection Authority, Environmental Department of Pavlodar Oblast Akimat and Office of Public Prosecutor of Pavlodar oblast. Permanent and most important subject of the discussion has been prevention of fishing from the mercury contaminated wastewater storage pond – Lake Balkyldak that poses a threat to health of Pavlodar population.

8.1.5.2. “Science based recommendations on arrangement of wastewater storage pond Balkyldak monitoring” and “Research Program of wastewater storage pond “Balkyldak” for making decision on further safe use of the lake” have been developed on the instruction of Pavlodar Oblast Akimat.

8.1.5.3. Scientific results of the monitoring works in Pavlodar were reported at the Annual Meeting of the American Institute of Chemical Engineers (AIChE) (Cincinnati, Ohio, USA, 30 October – 4 November, 2005) including the results of 2006 - (i) at the 8<sup>th</sup> International Conference “Mercury as a Global Pollutant” (Madison, Wisconsin, USA, the 6-11<sup>th</sup> August of 2006), (ii) at 29th AMOP Technical Workshop (Vancouver, Canada, the 6-8<sup>th</sup> of June), at seminars: (iii) BIOMERCURY in Prague, Czechia (18-19 May, 2006), in (iv) Oxford, UK (20-26 August, 2006) and (v) ISTC in Almaty (19-20 September, 2006) and published as proceedings of International Conference /1/ and the article in USA scientific journal /2/.

8.1.5.4. AIPET, BG Chair of Environmental Technology has arranged press-tour to inform public of Kazakhstan with the results of the first stage of Demercurization Program and also first results of the mercury monitoring for journalists of Kazakhstan at the former PO “Khimprom” on the 12<sup>th</sup> of July and press-conference – at Pavlodar Territorial Environmental Protection Authority. The results of the press-tour have been highlighted in news programs of four Republican TV channels (Khabar, 31<sup>st</sup>, Kazakhstan, Rakhat), two Pavlodar oblast TV channels (Kazakhstan-Pavlodar, Irbis) and also Radio 31. Publications on the results of the press-tour have

been located on the official websites: [www.inform.kz](http://www.inform.kz), [www.khabar.kz](http://www.khabar.kz), [www.kazpravda.kz](http://www.kazpravda.kz), [www.panorama.kz](http://www.panorama.kz), [www.31.kz](http://www.31.kz), [www.liter.kz](http://www.liter.kz), [www.expressk.kz](http://www.expressk.kz), [www.expert.kz](http://www.expert.kz), and also in 5 Republican and 6 regional newspapers and magazines /3-13/.

8.1.5.5. On the 16<sup>th</sup> of August a workshop on the preliminary results of mercury monitoring in the framework of ISTC K-1240 project was arranged for staff of environmental service, NGO and deputies of Pavlodar City at Pavlodar Territorial Environmental Protection Authority. The workshop activity was highlighted in news programs of two Republican (KTK, Kazakhstan) and two regional (Kazakhstan-Pavlodar, Irbis) TV channels.

## **8.2. Technical progress during the first year of the project**

### **8.2.1. Field works**

#### 8.2.1.1. Investigation of groundwater

Groundwater investigation has been carried out across all area of the Northern industrial site of Pavlodar in order to obtain data about seasonal variation of their level and then to use this material for simulation of hydrogeological conditions and also in places of mercury contamination with purpose to receive the data on total and methyl mercury concentration changes.

##### 8.2.1.1.1. Groundwater level measurements

Twice in July and September of 2006 groundwater level measurements were taken in 239 observation boreholes. The measurements were taken from boreholes' caps using a special tape-line having a plummet and clapper at the end. Separately measurements of height of borehole caps and their coordinating were performed with help of a portable GPS. The results of these seasonal measurements ("Summery table 03.2006") have been used to create the local model of groundwater mercury contamination.

##### 8.2.1.1.2. Groundwater sampling for their analysis for total and methyl mercury

Groundwater samples were being taken from 87 observation boreholes of the system of mercury monitoring at Northern industrial area of Pavlodar using a submerged electrical pump in June and July, 2006 according to the technique developed by AIPET in 2001-2002 and based on very careful rinsing of equipment for borehole pumping and on the rinsing quality control. Simultaneously with groundwater sampling measurements of its level, temperature and pH were taken.

Water samples were taken in duplicate into single-use plastic bottles without filtration and preservation (the taken samples were delivered to the laboratory twice a day). Coca-cola plastic bottles of 0.5 liter after dispensing the cola were used. Marks were put by an indelible marker on bottles full of coca-cola to indicate volume of the liquid in a bottle. Then coca-cola was poured out, empty bottles were screw-topped, put into clean plastic bags and delivered to sampling place. At the sampling place the plastic bags were opened slightly, bottles were tagged, opened, rinsed three times with groundwater and filled with groundwater up to the mark. After that the bottles filled with groundwater samples were screw-topped and enclosed within plastic bags (the same procedures were done for bottles with rinsing water). Before sampling triple volume of groundwater confined within a borehole cavity was pumped out of each observation borehole. After sampling the electric pump, electricity cables and pump hoses were taken out of the borehole and put into a special tank with capacity of 50 liters made of stainless steel. Sampling

equipment was being washed from caught-on mercury in the tank. For that the tank containing the equipment was filled up by fresh tap water which had been controlled for mercury absence (tap water was transported to groundwater sampling points in alumina tank of 2 m<sup>3</sup> using auto trailer), then rinsing water was pumped out of the tank with help of the rinsed pump and pump hoses. Such operation was repeated three times and then the clean equipment was delivered to next borehole inside of the same airtight stainless steel tank. Sampling quality control lay in chemical analysis of final portion of rinsing water for caught-on mercury after each equipment-washing operation (samples of rinsing water were taken without duplicating). All water samples and blanks were delivered to the chemical analytical laboratory not later than in 4 hours after sampling in an icebox holding the temperature of not higher than 10°C.

Groundwater samples for methyl mercury determination were taken in duplicate from three boreholes C69-02, C32-03 and P8 on the 21<sup>st</sup> of July, 2006 generally according to the same method as that for total mercury. The difference was that water samples for analyses for methyl mercury were taken into 1 liter one-use vodka glass bottles closed with metal screw-tops having plastic cover gaskets. The bottles were washed first with bromite-bromate mixture (see in Section 8.2.2) and then a few times with reagent water. The bottles were put an icebox just immediately after their filling up with water samples and delivered to the analytical laboratory of Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia. During stops on the way the samples were kept at the temperature of 4°C in stationary refrigerators. The samples were delivered to the laboratory on the 4<sup>th</sup> of August, 2006 and kept at 4°C in a fridge until being processed. Also two empty bottles washed with the same way were sent to the same laboratory as blanks.

#### 8.2.1.2. Investigation of soil mercury contamination

Investigation of soil mercury contamination was conducted in the site of 2002-2004 demercurization works in order to assess their efficiency and also in places of mercury contaminated groundwater possible wedging out and pastures mercury pollution.

##### 8.2.1.2.1. Investigation of mercury contamination of soil at the industrial area of former chlor-alkali production

19 soil samples were taken at the industrial area of the former chlor-alkali production and in the area of former 6<sup>th</sup> wastewater pumping station in July of 2006. The samples were taken in places of intensive mercury pollution (the map of mercury pollution with results of monitoring of 2001-2002 was used) from topsoil (0-10 cm) into duple one-use plastic bags. Sampling technique lay in following: first vegetative layer was removed in sampling points using a spade then topsoil was sliced off three times at angle of 45°, at that first two soil portions were thrown away and third one was taken as a sample. There was no quality control of the topsoil sampling. Sampling points were coordinated with help of portable GPS. Bags with samples were tagged and delivered to AIPET laboratory in Almaty.

Also efficiency of demercurization works at the industrial area of former chlor-alkali production, at the area of former 6<sup>th</sup> wastewater pumping station and special storage ponds for solid and liquid mercury wastes was estimated with help of analysis of near-earth air (10 cm of ground surface) in 20 points for mercury vapors content. The measurements were implemented on the 21<sup>st</sup> July, 2006 since 3 am till 6 pm at the air temperature of 27°C (Summary table 022006) in cooperation with specialists from AO GEOTestBRNO (Brno, Czechia) using portable mercury atomic absorptive spectrophotometer (AAS) Lyumex RA 915+ (Russia) according to the method of the instrument manufacturer.

#### 8.2.1.2.2. Investigation of soil mercury contamination in places of mercury contaminated groundwater possible wedging out

Previously the soil sampling plan was prepared on the regular grid based on GIS of the Northern industrial area of Pavlodar for five places of mercury contaminated groundwater possible wedging out at the territory between the 1<sup>st</sup> industrial site of Pavlodar Chemical Plant and the wastewater storage pond – Lake Balkyldak.

In September, 2006 111 soil samples were taken from topsoil (0-10 cm) of this area on the regular grid for total mercury determination (the sampling method is described in the Section 8.2.1.2.1.).

#### 8.2.1.3. Investigation of mercury pollution of wastewater storage pond – Lake Balkyldak

Investigation of mercury pollution of wastewater storage pond – Lake Balkyldak lay in investigation of bottom sediments of the Lake and its biota.

##### 8.2.1.3.1. Estimation of bottom sediments mercury pollution of wastewater storage pond – Lake Balkyldak

Before the plan of bottom sediment sampling was prepared on the regular grid based on GIS of the Northern industrial area of Pavlodar for 200, 150, 100 and 50 sampling points which could be corrected at the site depending on complexity and time of field work carrying out.

Winter field works was conducted in March 2006 after the air temperatures had gone up to – 10°C. These works was interrupted at the end of March after the ice surface started cracking intensively when the temperature had elevated 0°C. In winter of 2005/2006 the ice thickness on the storage pond Balkyldak reached 0.6 – 0.9 m. It allowed using cars with cross-country capacity to move across the surface (the area of about 23 km<sup>2</sup>) of the lake. However snowdrifts made the field works very difficult in places of reed thickets. During a month of the field works they managed to realize with little excess the regular sampling plan for 50 sampling points (excluding sampling points where it was impossible to take bottom sediments because of ice reaching the bottom; such samples were taken in summer time). In total 107 bottom sediment samples have been taken from 52 sampling points through the holes drilled through the ice with help of samplers of two different constructions: soft sediments were taken layerwise at 50 cm intervals, clay samples were taken from surface bottom layer to the depth of 25 cm. Using the samplers it was possible to take ground at pond's depths down to 12 m (bathymetric and soft sediment capacity measurements were being done simultaneously with sampling). Coordinates of sampling points were determined with help of hand-held GPS with maximum error of 7 m. The samples were taken into throwaway linen bags which in turn were packed together with an identification tags into new double plastic bags. After each sampling the equipment was cleaned thoroughly of remaining snow or water from the storage pond (Quality control of the clean-up was not conducted). The samples were delivered to Almaty at the beginning of April and dried to air-dry state at room temperature in aerated, warm and clean room (plastic bags were opened, but linen bags remained closed). Further dry bottom sediments have been kept in the same packing where they were put in at sampling and were being dried.

Summer bottom sediment sampling was conducted in July 2006. 33 samples from 17 not very deep sampling points located near the shoreline of wastewater storage pond Balkyldak were taken. The samples were taken from a boat board into tagged double plastic bags similar to the winter sampling (bottom sediment sampling far from the shore was impeded due to strong



waving and the equipment bulkiness). After each sampling the equipment was being cleaned very carefully with the lake water from caught-on sediments (there was no the cleaning quality control). The samples were frozen and delivered to AIPET Laboratory in Almaty where were stored frozen.

Bathymetric measurements and measurements of soft sediments thickness were carried out (“Summary table 01.2006) simultaneously with bottom sediment sampling and used to develop GIS of the Northern industrial area of Pavlodar.

#### 8.2.1.3.2. Sampling of biota of both wastewater storage pond Balkyldak and control pond

Summer sampling of aquatic life of pond Balkyldak was conducted in June-August, 2006. There were taken: silver crucian – 86 samples (including 30 samples for morphological analysis and 56 samples for chemical analysis); carp – 1 sample (for chemical analysis); Shellfish, benthos and plankton – 1, 4 and 2 samples respectively for both chemical analysis for total mercury content and morphological analysis.

Fish were caught by either fixed nets with mesh of 30-65 mm or fishing rods. Samples of plankton were taken by Apshtein plankton net and tuck net of gas-sieve at sample stations. Samples of benthos were taken from bottom sediments which were taken on the shore and rinsed many times at the sample stations. Species belonging was not determined. Shellfish were taken by hands from the ground and water plants. Also empty shells were taken for morphological study. Samples for chemical analysis for mercury were frozen and delivered to AIPET Laboratory in Almaty.

Ichthyologic research was carried out according to standard instruction on fish study. Morphological characteristics were obtained by beam compass measuring with accuracy of 0.5 mm.

On the 10-11<sup>th</sup> August, 2006 capture of silver crucian (30 samples) for morphological analysis was done from the control pond – Lake Krivoe of Kachirskiy region (water-surface area is 8 ha, depth - 1-4 m, eutrophication – 95%, water recharge is from Irtysh River floods, ichthyo-fauna consists of crucian, roach, pike and perch).

#### 8.2.2. Chemical analytical works

Groundwater analyses for total mercury content were carried out in the laboratory building provided by AO “Kaustik” at the territory of former “Khimprom”, Pavlodar using equipment delivered from Almaty.

Groundwater analyses for methyl mercury content were conducted in an analytical laboratory of Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia.

The rest chemical analytical works were done in AIPET Laboratory in Almaty. All operations on samples preparation and their analysis for mercury content were conducted using minimum of laboratory glassware (one-use if possible) and reagents in order to decrease probability of samples pollution.

*Technique of determination of total mercury content in water samples based on: PS Analytical. Customer Technical Information File, Issue No. 4.2, Issue Date: November 2 2000: “Mmhwat, Millennium Merlin method for total mercury in drinking, surface, ground, industrial and domestic waste waters and saline waters”. QA/QC was carried out in accordance with US EPA*

method 1631 rev E: “Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry”, August 2002. The difference lay in using one-use polyethylene tetrathalate (PET) coca-cola bottles for samples storage instead of recommended reusable PS Analytical containers made of fluoropolymer, borosilicate glasses or polypropylene of high density. Special study undertaken earlier showed that mercury losses were statistically negligible when storing water samples with similar salt composition in PET bottles without preservatives during a day.

Coca-Cola bottles of 0.5 l containing water samples were taken out of plastic bags immediately after their delivery to the laboratory, rinsed with distilled water after that samples were decomposed at once. Before the decomposition 100 ml of sample were poured out of the bottle. Then 60 ml of 33% solution of hydrochloric acid and 4 ml bromide-bromate mixture (0.4 N solution of potassium bromide and 0.4 N solution of potassium bromate at a ratio of one to one) were added into the bottle to the rest 400 ml of the water sample. Solution in bottles had to become of yellow color. If solution in some bottles did not colored or lost the yellow color after 30 minutes than 50 ml aliquot was taken from such bottles, put into new Coca-Cola bottle and diluted 10 times with blank solution.

Next day 0.24 ml of 12 % solution of hydroxylamine hydrochloride were added into the bottles with samples; the bottles were shaken and total mercury content was determined using the atomic fluorescence spectrophotometer (AFS) “Millennium Merlin” 10.025 (UK).

*Technique of determination of methyl mercury content in water samples* lay in the following: Approximately 70 ml of sample was weighed directly in a 125 mL Teflon bottle. After addition of 5 mL of conc. HCl and 30 mL of CH<sub>2</sub>Cl<sub>2</sub>, the bottles were closed and shaken over night. Water phase was then removed with water pump and approximately 40 mL of Milli-Q water was added to the CH<sub>2</sub>Cl<sub>2</sub>. Organic phase was evaporated on water bath at about 90°C. Samples were then purged with N<sub>2</sub> for 5 minutes to remove remaining CH<sub>2</sub>Cl<sub>2</sub>. This extraction was repeated twice. An aliquot of the aqueous sample was added to Teflon reaction vial and pH was adjusted to be 4.6 with addition of 100 µL of acetate buffer. 50 µL of 1% NaBEt<sub>4</sub> was added in the reaction vial at the end and the mixture was left to react at the room temperature for 15 minutes. Ethylated MeHg as ethylmethylmercury was purged onto Tenax trap for 15 minutes with Hg-free nitrogen. Tenax traps were then connected to the flow of argon and MeHg was thermally desorbed (180°C) onto isothermal GC column. Hg species were converted to Hg<sup>0</sup> by pyrolyses at 600°C and measured by cold vapour atomic fluorescence detector (CVAFS). The limit of detection, calculated on basis of three standard deviation of blanks, was about 10 pg MeHg/L. (3,4,5).

The reproducibility of the method is 5 to 10%. Estimated uncertainty with a coverage factor k=2 was 9.1%.

Recovery of MeHg was estimated by spiking the samples with known amount of MeHg prior extraction and analysis and have shown to be between 85 to 90 % therefore recovery factor was used in the calculation of the results. During each batch of sample analysis 2 blanks ( reagent blank plus the sample processing blank) were also analysed in order to avoid uncontrolled contamination.

*Technique of mercury determination in soils and bottom sediments* was based on: (i) PS Analytical. Customer Technical Information File, Issue No. 4.2, Issue Date: November 2 2000: “Mmhgslud, Millennium Merlin method for mercury sludge, soils and sediments”, and (ii) US EPA Appendix to Method 1631: “Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid

Digestion and BrCl Oxidation”, January 2001. Quality control was done in compliance with instruction (ii).

Dried and ground soil sample was weighted (about 1 g) and put into 100 ml beaker having also a point of 50 ml. 15 ml of concentrated hydrochloric acid and then 5 ml of concentrated nitric acid were carefully added to the beaker, which then was covered with a watch crystal with one-use gasket of polyethylene film and heated carefully at the temperature of 95°C on a water bath until getting even boiling. After the solution cooling the volume in the beaker was increased up to 50 ml with reagent water. In order to remove nitrogen oxides 5 ml of 12% solution of hydroxylamine hydrochlorid were added into the beaker, stirred carefully and given time for the solution getting transparent. Before measurement 10 ml of sample were taken out of the beaker and placed into volumetric flask and diluted up to 100 ml with reagent water. An aliquot was taken out of the solution, diluted with blank solution to necessary concentration level and mercury content was measured using AFS “Millennium Merlin” 10.025 (UK).

In total 270 water samples, 140 bottom sediment samples and 27 soil samples have been analyzed for total mercury and 3 water samples – for methyl mercury.

The results of analysis of water for total and methyl mercury and soil and bottom sediments for total mercury were used to produce a database (“Summary tables 05.2006, 06.2006, 07.2006 and 08.2006”).

It must be mentioned that the results of the analyses for total mercury of water samples taken from the same three boreholes but at 10 days interval obtained in the analytical laboratories of AIPET and Jožef Stefan Institute, Ljubljana, Slovenia (“Summary tables 05.2006 and 06.2006”) differ from each other not more than by 15 %, that is good coincidence. The results for methyl mercury obtained in the analytical laboratory of Jožef Stefan Institute, Ljubljana, Slovenia for water samples taken from the same two boreholes but at one year interval (in 2005 and 2006) differ by 50-70%. Such a big difference came most likely from the fact that for water analysis for methyl mercury procedure of water sampling and the samples transportation were incorrect in 2005 (water samples were taken into plastic bottles, preserved by hydrochloric acid and being transported to the laboratory for 2 months without cooling).

### **8.2.3. Office study**

#### 8.2.3.1. Database creation

Electronic summary tables (Summary tables 01-08.2006) were compiled to form the database of post-demercuration monitoring.

#### 8.2.3.2. Development of GIS of Northern industrial area of Pavlodar (see Q(II))

GIS of the Northern industrial area of Pavlodar produced earlier in 2000-2001 has been made more detailed and completed with new data from satellite images and archival documents and also from direct measurement with help of portable GPS: vegetation boundary and the bottom contour have been input *at the area of wastewater storage pond – Lake Balkyldak*, its nowadays shore line has been made more correct; outline of impervious barrier so called cut-off wall *at the industrial area of the former chlor-alkali production* has been made more precise.

#### 8.2.3.3. Analysis of the results of investigation of groundwater mercury contamination

The results of determination of mercury concentration in groundwater at the area of mercury pollution (“Summary table 05.2006) have been inserted onto the vector map together with the results of similar research of 2004 and 2005 (Fig.1, Annex 1). Together with Table 1 (Annex 1) this map shows dynamic of total mercury concentration change in groundwater in post-demercuration period and allows finding spots with increase in mercury concentration at the area of groundwater mercury contamination plume (due to natural drift of the plume of mercury contamination along groundwater flow) and also spots with decrease in mercury concentration near former building 31 (due to cessation of groundwater recharge with mercury from the source of contamination contained by the cut-off wall). Considerable decrease in mercury concentration near the main hot spot of the mercury contamination allows drawing preliminary conclusion about sufficient efficiency of the taken measures on isolation of the source of mercury contamination located under the former building 31 from groundwater.

The results of determination of methyl mercury concentration in water taken from three boreholes within the plume of mercury pollution (“Summary table 06.2006”) range from several ng/l to tens of ng/l that averages 0.01% of total mercury concentration.

#### 8.2.3.4. Analysis of the results of investigation of soil mercury contamination

The results of determination of mercury concentration in soil samples taken within the industrial area of former chlor-alkali production and in site of 6<sup>th</sup> wastewater pumping station (“Summary table 07.2006) has shown that in general high levels (from 2.1 to 95.1 mg/kg) of soil mercury contamination (at maximum permissible concentration of mercury in soil - MPC<sub>s</sub> being 2.1 mg/kg) keep up here after implementation of demercuration works both on the surface of clay screens covering concrete foundation of demolished buildings and within the territory where digging were conducted including excavation of highly contaminated topsoil. To the maximum these concentrations could be in the order of g/kg.

Respectively mercury vapors concentrations in the surface air (“Summary table 02.2006”) ranged from 100 to 1600 ng/m<sup>3</sup> (the average daily maximum permissible concentration in atmosphere MPC<sub>ad</sub> equal to 300 ng/m<sup>3</sup> was exceeded in 7 of 16 sampling points). Also extremely high mercury vapors concentrations (above the maximum permissible mercury concentration for a working area which is 10000 ng/m<sup>3</sup>) were found (in one measuring point) at the place where the clay covering over the concrete foundation of the building 31 had been destroyed by atmospheric precipitation.

Preliminary results showed persistent high risk for working personnel posed by both soil mercury contamination within the former chlor-alkali production and insufficiency of measures on its clean up carried out on the Program of Demercuration in 2002-2004. Persistent soil mercury contamination can in turn entail additional entrance of dissolved mercury into groundwater due to infiltration of atmospheric precipitation through the contaminated layer because this contamination extends beyond the area confined by the cut-off wall. All this necessitates carrying out more detailed investigation of mercury contaminated topsoil within the industrial area of the plant in the framework of K-1240 project resulting in production of new map of the contamination (see Section 9). Both administration of the plant and local authority have also shown their interest in conducting more detailed in comparison with 2000-2002 study of the soil mercury contamination within the industrial area of the former PO “Khimprom” caused by expected revival of chemical productions and necessity of risk assessment for personnel which will work at this territory.

Measured concentrations of mercury vapors which were about 200 ng/m<sup>3</sup> (on two measuring points) in the center of the landfill for building structures (50 m to the south from the former

building 31) and from 100 to 200 ng/m<sup>3</sup> (on four measuring points) on site of special ponds for solid and liquid mercury waste located at south shore of wastewater storage pond Balkyldak proved quite good containment of the mercury waste by these engineering structures.

#### 8.2.3.5. Analysis of the results of the bottom sediment investigation of wastewater storage pond – Lake Balkyldak

In April, 2006 and October, 2006 two scenarios of computer maps of depths and thicknesses of bottom sediments of the storage pond - Lake Balkyldak have been produced within GIS of the Northern industrial area of Pavlodar based on the data from Summary table 01.2006 using software ArcGIS, module Spatial Analyst. The second scenario of the map (Fig.2, Annex 1) differs from the first one (Fig.9, Technical Report for Quarter II on K-1240 project) in increase by 1/3 in number of depth and bottom sediment thickness measuring points (due to summer field works) and in using “Spline” method instead of “Inverse distance weighted (IDW)” method for interpolation (in the second case the picture on the bottom sediment thickness map correlated better with the picture on the bathymetric map, however the final variant of the method of interpolation will be chosen after measuring on the rest 131 measuring points).

Figure 2 shows that the most part of the water space of the storage pond is not able to accumulate considerable amount of bottom sediments because of not great depth of the pond and intensive waving activity over the vast area (23 km<sup>2</sup>) of the water surface. Accumulation of bottom sediments of the pond (up to the soft sediment thickness of 1.6 m) occurs in general in one of its two the deepest depressions (down to 9.5 m) located in site of former natural salt Lake Balkyldak (area I) and contained old bottom sediments of this lake. There is mainly the bed movement and increase in the basin depth in site of the second natural Lake Sheptykol’ (area II).

The results of determination of mercury concentration in bottom sediment samples (“Summary table 08.2006) have been used to create preliminary vector map “Mercury contamination of bottom sediments of wastewater storage pond Balkyldak” and to do the calculation on this basis of amount of mercury deposited in the bottom sediments of the pond which has come to 135.0 tons. As expected south-west part of the pond turned out to be the most contaminated one because there was outfall of all sewer wastewater of PO “Khimprom”, Pavlodar in this place. Moreover its most extensive depression lies at the same place. However high level (on a considerably smaller scale though) of contamination is also observed in the second depression of the storage pond (area II) due to the sediment movement caused by waving activity (including scour of the bottom sediment at shallow water).

The produced computer maps of the wastewater storage pond – Lake Balkyldak and calculations will be made more accurate in early spring of 2007 after bottom sediment sampling from the rest 150 scheduled sampling points.

#### 8.2.4. Computer simulation

The first stage of creation and calibration of the local hydro-geological model of the area of groundwater mercury contamination within the former PO “Khimprom” has been completed. The purpose of the works was to make the prognoses of mercury contaminated groundwater spread more exact due to taking into account the processes of mercury sorption/desorption by water bearing strata and also to study possible interconnection between waters of Lower-middle-Pliocene deposits of Pavlodar series and Oligocene deposits of Nekrasov series. Proportion of

boundaries of the regional and local models in horizontal projection is shown on the Fig. 4, Annex 1.

In order to achieve the purpose additional archival data have been collected, reconnaissance investigations have been conducted, hydro-geological conditions within the local model have been made more exact, schematization of hydro-geological conditions has been carried out, input data have been prepared in proper formats, local hydro-geological model has been produced by means of software GMS 6.0 and its calibration has been done.

On bases of the collected data 20 detailed hydro-geological cross sections have been constructed in the sub latitudinal and sub meridional directions. The cross sections are shown on the Fig.4. Three dimensional diagram depicted lithologic structure of the simulated area is shown on the Fig.5, Annex 1. Based on hydro-geological cross sections the model of stratigraphy has been produced by means of software GMS 6.0.

The simulated area in section is schematized as 19 layers (regional model consists of 5 layers). In horizontal projection it is approximated by orthogonal grid with step of 40 m (on the regional model the grid step ranged from 50 to 200 m in the area of the plume of contamination spread) and the block size of 113 x 92. Groundwater heads changing with time were established on outer boundaries of the local model which corresponded to groundwater heads obtained on the regional model of the Northern industrial area of Pavlodar.

The inverse stationary task has been solved with the purpose of calibrating the model. Position of groundwater level as of 1970 i.e. conditionally undisturbed period was reproduced in the model. Filtration coefficients of water bearing strata and value of groundwater infiltration recharge have been made more precise. Average error of the solution has been not more than 1 cm. The result of the inverse stationary task solution is represented on the Fig.6, Annex 1.

## **9. Current technical status of the project**

The works are carried out in general in compliance with the schedule because the most activity falls at seasonal field works and their non-fulfillment at the proper time entails necessity to abandon the efforts at all. Most of work on oil products monitoring had to be suspended. The reasons are described in the section 11 of this report. In future it is inexpedient to resume these works on a scheduled scale within the framework of K-1240p project because it would threaten with failure to carry out the works on mercury monitoring where the schedule is very intensive.

The Work Plan for the second and third year is supposed to be changed so that:

1. Participating Institute PCP/Kaustik in cooperation with AIPET would conduct investigation of soil mercury contamination at the industrial area of the plant and at the territory adjacent from the north and also computer map of topsoil mercury contamination would be produced (see the section 8.2.3.4 of this report) instead of scheduled oil products monitoring. At the same time measurements of mercury vapors concentrations in both soil air and near-earth air is intended to be done at the same soil sampling points at different weather conditions using hand-held atomic absorptive spectrophotometer (AAC) Lumex RA 915+ (which would be acquired instead of scheduled equipment for oil products determination). Such an investigation and following comparison of the maps of soil contamination by elemental mercury and the maps of mercury vapor concentrations in soil/near-earth air can be a ground for development of new method of express-monitoring of topsoil metallic mercury contamination.

2. Participating Institute IHH would simulate both efficiency of different technologies of groundwater clean up from mercury within the plume of contamination using the local model and also different scenarios of interception of groundwater flow going from joint ash lagoon of power plants (TEs) 2 and 3, recharging wastewater storage pond –Lake Balkyldak and flooding industrial enterprises of the Northern industrial area of Pavlodar instead of simulation of groundwater contamination by oil products. Such simulation could be done in cooperation with Integrated Pollution Management, Knowledge Transfer Network (IPM-NET), University of Oxford as it was suggested at the Workshop on Mercury and Environmental Protection at Pavlodar, Kazakhstan (Oxford, UK, 20-26 August, 2006).

3. Participating Institute BMP would conduct monitoring of oil products on a reduced program mainly at the territory of Pavlodarskoe village during two next years using wells of local population. Stepnogorsk Laboratory of Monitoring can carry out chemical analysis of oil products using their own equipment. Also this Participating Institute could investigate spread of underground spot of oil products contamination according to the method developed by AIPET in 2004 (see the section 8.1.3.2 of this report and Technical report on K-1240 project for Quarter IV, the section 1.1.2.4)

At the workshop “Mercury and Environmental Protection at Pavlodar, Kazakhstan” in Oxford University (Oxford, United Kingdom, 20-26 August, 2006) English scientists suggested to distinguish organic and inorganic forms of mercury in the course of monitoring because these forms differ very much in their toxicity and hazard for environment and local population. Methyl mercury is the most dangerous form which can be generated in significant amount in surface water and groundwater as well as in bottom sediments.

It is suggested to broaden the scope of monitoring works conducted on ISTC K-1240 project by including investigation of methyl mercury content in mercury contaminated groundwater and wastewater storage pond – Lake Balkyldak as a new separate **Task 6**. However such broadening of the Work Plan of ISTC K-1240 project requires approval of the western partner (US EPA) because it should be supported by increasing in funds (including for purchase of additional analytical equipment and training for two of the staff in a chemical analytical laboratory in Slovenia for two months) and entail the project prolongation.

## **10. Cooperation with foreign collaborators**

During the first year of K-1240 project there have been three meetings with foreign partner Paul Randall (two meetings in USA in Cincinnati, Ohio in November, 2005 and in Madison, Wisconsin in August, 2006 and one meeting in Kazakhstan in Almaty and Pavlodar in September, 2006) and three meetings with foreign collaborator Trevor Tanton (two meetings in Kazakhstan in Almaty in January and September, 2006 and one meeting in United Kingdom in Oxford in August, 2006). The Work Plan of K-1240 project, its progress and first results obtained were being discussed during the meetings. Trevor Tanton is one of the initiators of including monitoring of methyl mercury into the Work Plan which is the most important and toxic mercury form (see the section 9). He also suggested the list of equipment necessary for fitting out a laboratory so that it can be possible to conduct analyses of nature waters and bottom sediment for methyl mercury there.

The paper about mercury pollution in Pavlodar, Kazakhstan issued in an American scientific journal /1/ has been prepared together with Paul Randall and the summary of the report at an International Scientific Conference /2/ held in Madison, Wisconsin, US in August, 2006 -with Paul Randall and Trevor Tanton. Besides Paul Randall advised and rendered his assistance in purchasing GMS 6.0 software for simulation of hydro-geological processes.

Joint attendance to conferences and workshops:

With Paul Randall:

1. Annual Meeting at the American Institute of Chemical Engineers (AIChE) (Cincinnati, Ohio, US, 30 October – 4 November, 2005),
2. 8<sup>th</sup> International Conference “Mercury as a Global Pollutant” (Madison, Wisconsin, USA, the 6-11<sup>th</sup> August of 2006),
3. ISTC Workshop “Commercialization of the results of scientific and technical developments in Kazakhstan (Almaty, 19-20 September, 2006)

With Trevor Tanton:

4. Workshop “Mercury and Environmental Protection at Pavlodar, Kazakhstan” (Oxford, United Kingdom, 20-26 August, 2006).

## **11. Problems encountered and suggestions to remedy**

The main problems resulted from insufficient involvement of two of Kazakhstan Participating Institutes into the work on K-1240 project: PCP – because of bankruptcy of the plant, dismissal of most of its staff and protracted procedure of its asset sale and BMP – because of reorganization of the management system of Stepnogorsk Laboratory of Monitoring and death of its head Alexandr N. Kosinov. Participation of the third Participating Institute PSU in the field works on the project also required considerable efforts of AIPET team because PSU team had not had experience in scientific projects and could not arrange their field works for a long time.

All this has resulted in overburdening AIPET team with field and chemical and analytical works and in turn in overspending AIPET’s travel funds for conducting expeditions and in reducing the scope of scheduled works in comparison with those in the Work Plan especially related to monitoring of groundwater oil products contamination (Task 2).

Due to failure of some Participating Institutes in adherence to the Work Plan schedule the correction of the Work plan for the second and third year of K-1240p project (see the section 9) is necessary to provide for in the sixth Quarter, which would reflect a real interaction of the participants in the work on the project.

## **12. Perspectives of future developments of the research developed**

The results of the first year of the project have shown the importance of monitoring research to evaluate demercurization works conducted in 2002-2004 and current status of mercury pollution in Pavlodar and mainly to plan further pollution management. If mercury deposits found in bottom sediments of the wastewater storage pond – Lake Balkyldak was predictable then level of soil contamination at the former chlor-alkali production and dynamic of mercury concentration change in groundwater turned out to be unexpected. Necessity to broaden and carry on the monitoring works in Pavlodar and to bring the work to the stage of risk assessment for the local population was emphasized at the Workshop “Mercury and Environmental Protection at Pavlodar, Kazakhstan” hosted by Oxford University (Oxford, United Kingdom, 20-26 August, 2006). However the research specified in K-1240 project is confined by finance recourses and



time and what is the most important - absence of institutional capacity to conduct the monitoring works. The task to establish “*Regional Monitoring Research Center*” (including a chemical and analytical laboratory) at the territory of former PO “Khimprom”, Pavlodar has been very urgent yet. Success in K-1240 project completion will be in general the result of success in creation of such Center and the laboratory in Pavlodar.

### **13. List of papers and reports published**

1. M. Ilyushchenko, P. Randall, T. Tanton, A. Akhmetov, R. I. Kamberov, L. Yakovleva. Activities to contain mercury pollution from entering the river Irtysh in Pavlodar, Kazakhstan. Paper S-285, in: Abstracts of Eighth International Conference on Mercury as a Global Pollutant (Madison, Wisconsin; August 6-11, 2006). DEStech Publication, Inc., 2006.
2. P. Randall, M. Ilyushchenko, E. Lapshin, L. Kuzmenko. Case Study: Mercury Pollution Near a Chemical Plant in Northern Kazakhstan. *The Magazine for Environmental Managers*, N2, 2006, P. 19-24.
3. Crucian of mercury lustre. *Kazakhstanskaya Pravda*, 11 August, 2006.
4. Realization of the Program of Mercury Monitoring has been started in Pavlodar. *Panorama*, 14 August, 2006.
5. Be caught double-headed fish. *Liter*, 14 July 2006.
6. Prisoner of underground sarcophagus. *Экспресс К*, 15 июля 2006.
7. Fate of the industrial city. *Ekspert Kazakhstana*, 24-30 July 2006.
8. Mercury has already not dangerous, but there is still underground control of it. *Zvezda Priirtyshiya*, 15 July 2006.
9. Mercury is under the control. *Sobytiya Nedeli*, 13 July 2006.
10. Once again about mercury ... *Region.kz*, 14 July 2006.
11. Mercury is entombed. What next? *Obozrenie nedeli*, 14 July 2006.
12. Mercury mine. *Versiya*, 17 July 2006.
13. Traces of Mercury. *Gorodskaya Gazata*, 19 July 2006.

## ANNEX 1: Illustrations attached to the main text

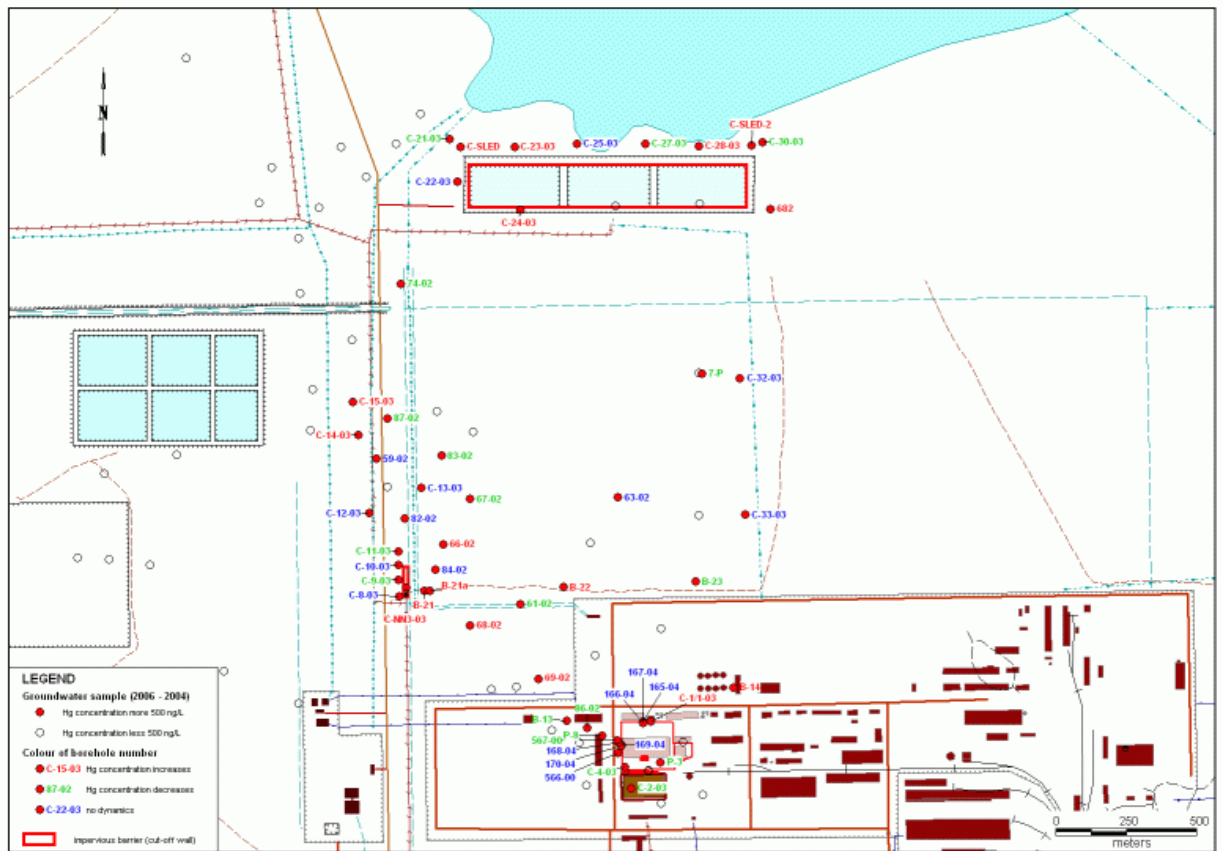


Fig.1. Dynamic of total mercury concentration change in groundwater of Northern Industrial Area of Pavlodar

Table 1

Dynamic of total mercury concentration change in groundwater of Northern Industrial Area of Pavlodar (on the results of mercury monitoring of 2004-2006)

NN	Borehole name	Total mercury concentration, ng/l 2004	Total mercury concentration, ng/l 2005	Total mercury concentration, ng/l 2006
1	C-16-03	129		144
2	C-17-03	223		171
3	C-18-03	36		46
4	C-19-03	175		229
5	C-20-03	97		140
6	<b>C-21-03</b>	4425		1630
7	<b>C-SLED</b>	3195		not able to pump
8	<b>C-22-03</b>	1400		1200
9	<b>C-24-03</b>	2995		not able to pump
10	C-26-03	19		not able to pump
11	C-29-03	58		not able to pump
12	<b>C-30-03</b>	45250		23500
13	<b>C-SLED-2</b>	90650		not able to pump
14	<b>C-28-03</b>	5390		not able to pump
15	<b>C-23-03</b>	648		not able to pump
16	<b>C-25-03</b>	2455		2180
17	<b>C-27-03</b>	24450		12500
18	<b>C-15-03</b>	1625		11800
19	<b>C-14-03</b>	2875		7450
20	<b>C-13-03</b>	6175		4700
21	<b>C-11-03</b>	29550		16400
22	<b>C-12-03</b>	28850		31500
23	<b>C-8-03</b>	35400		43500
24	<b>C-9-03</b>	27200		17600
25	<b>C-NN3-03</b>	6025		not able to pump
26	C-34-03	80		86
27	<b>C-35-03</b>	171		737
28	<b>C-33-03</b>	943		941
29	<b>C-32-03</b>	43850		40600
30	<b>63-02</b>	5050		3950
31	62-02	35		21
32	C-6-03	21		138
33	<b>84-02</b>	28850		30800
34	<b>67-02</b>	854		493
35	<b>83-02</b>	798		493
36	72-02	69		44

37	90-02	140		140
38	<b>74-02</b>	1435		338
39	<b>87-02</b>	9315		6150
40	70-02	105		307
41	<b>73-02</b>	479		744
42	<b>79-02</b>	126		919
43	55-02	50		59
44	89-02	76		38
45	<b>88-02</b>	468		504
46	<b>682</b>	3160		not able to pump
47	P-6	50		10
48	565-00	29		52
49	522-00	<5		<5
50	78-02	32		111
51	81-02	14		9
52	<b>566-00</b>	3055		5100
53	<b>86-02</b>	1775		287
54	85-02	6		<5
55	P-1	23		83
56	6-P	39		29
57	5-P	12		<5
58	C-5-03	121		160
59	<b>C-4-03</b>	517		354
60	<b>P-3</b>	24700		14700
61	<b>C-2-03</b>	137000		36500
62	<b>C-1/1-03</b>	2135		5600
63	<b>B-22</b>	1255		4780
64	8-P	<5		not able to open
65	<b>7-P</b>	3875		2490
66	<b>B-23</b>	946		442
67	C-1-03	212		not able to pump
68	<b>B-14</b>	4030		not able to pump
69	<b>B-13</b>	2845		724
70	P-4	159		72
71	75-02	166		364
72	76-02	8		<5
73	<b>83-02</b>	765		493
74	<b>61-02</b>	17600		5420
75	<b>B-21</b>	12150		27300
76	60-02	15		not able to pump
77	<b>C-10-03</b>	41300		39300
78	<b>B-21a</b>	126000		destroyed
79	<b>567-00</b>	47000		23400
80	<b>P-8</b>	102750	18000	14200
81	<b>82-02</b>	57550		44600
82	<b>66-02</b>	85300		167000
83	<b>59-02</b>	41100		32400
84	<b>C-2-03</b>	134750		36500
85	<b>68-02</b>	36700		57200
86	<b>69-02</b>	153500	165000	154000

87	29-P	not observed		449
88	<b>165-04</b>	not observed		<b>10500</b>
89	<b>166-04</b>	not observed		<b>3380</b>
90	<b>167-04</b>	not observed		<b>3310</b>
91	<b>169-04</b>	not observed		<b>28200</b>
92	<b>170-04</b>	not observed		<b>6880</b>
93	<b>168-04</b>	not observed		<b>7220</b>
94	171-04	not observed		270
95	162-04	not observed		295
96	164-04	not observed		123
97	529	not observed		44
98	64-02	not observed		7
99	93	not observed		71
100	77-02	not observed		<5
101	92	not observed		11

Comments to the table 1: “Borehole name” column: **red** borehole names indicate increase in mercury concentration, **green** – decrease in mercury concentration, **blue** – absence of any dynamics; “Total mercury concentration” column: **red** figures indicate exceeding the sanitary standard (500 ng/l).

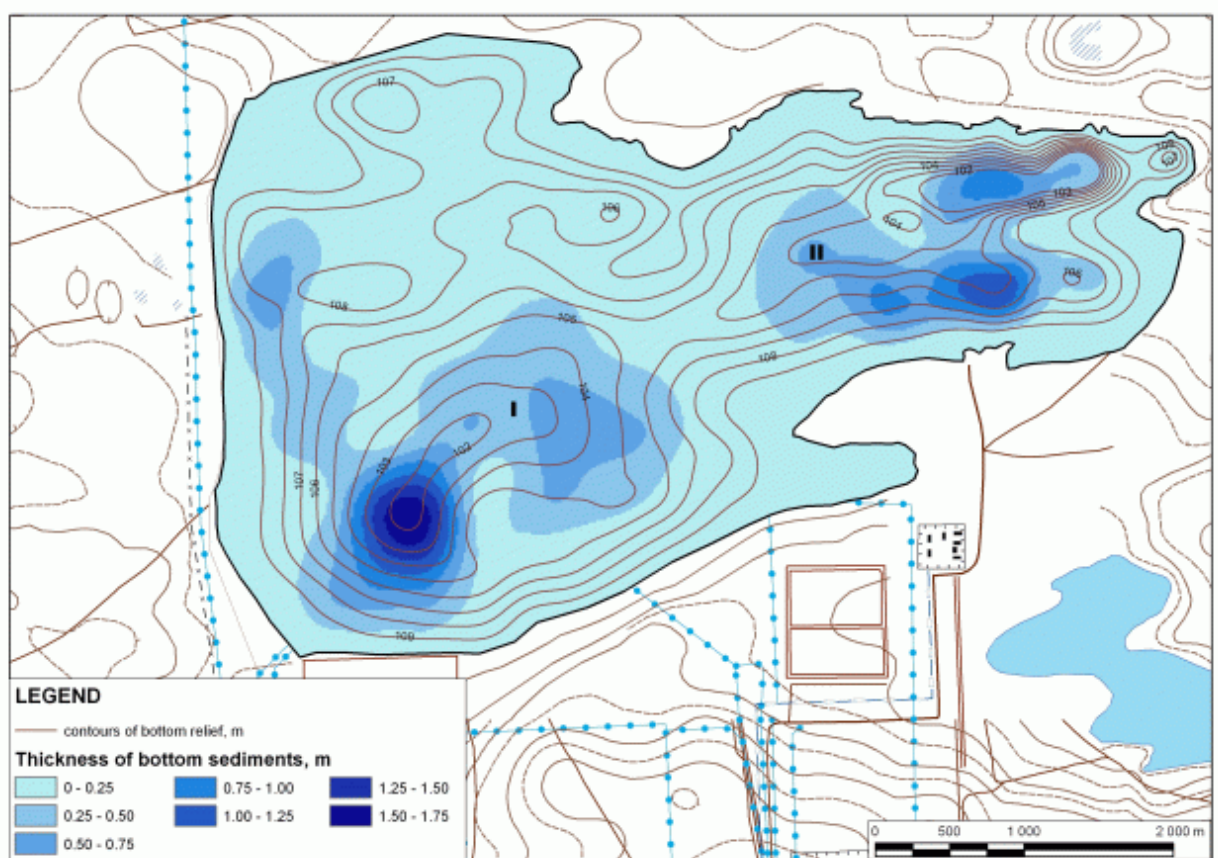


Fig.2. Map of depths and thickness of bottom sediments of wastewater storage pond – Lake Balkyldak

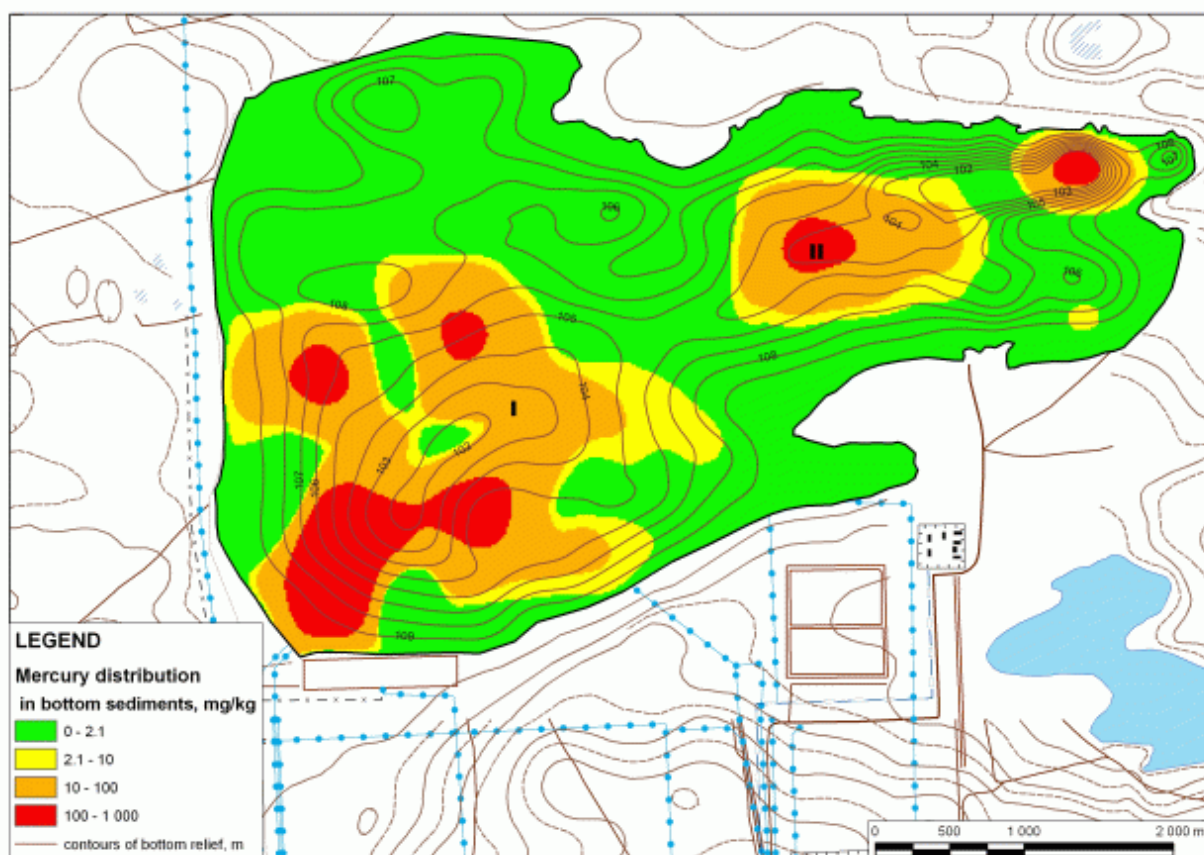


Fig.3. Map of bottom sediments contamination of wastewater storage pond – Lake Balkyldak

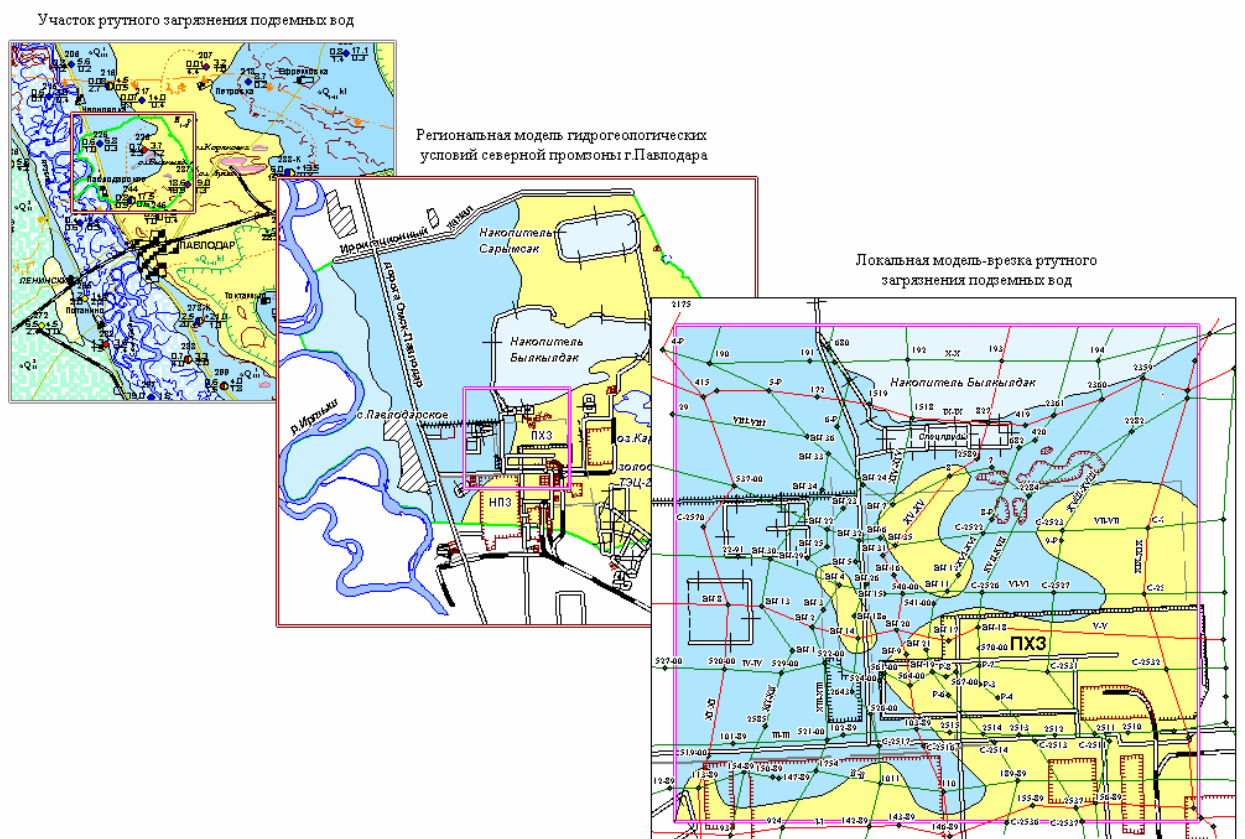


Fig.4. System of hydro-geological models of Northern Industrial Area of Pavlodar



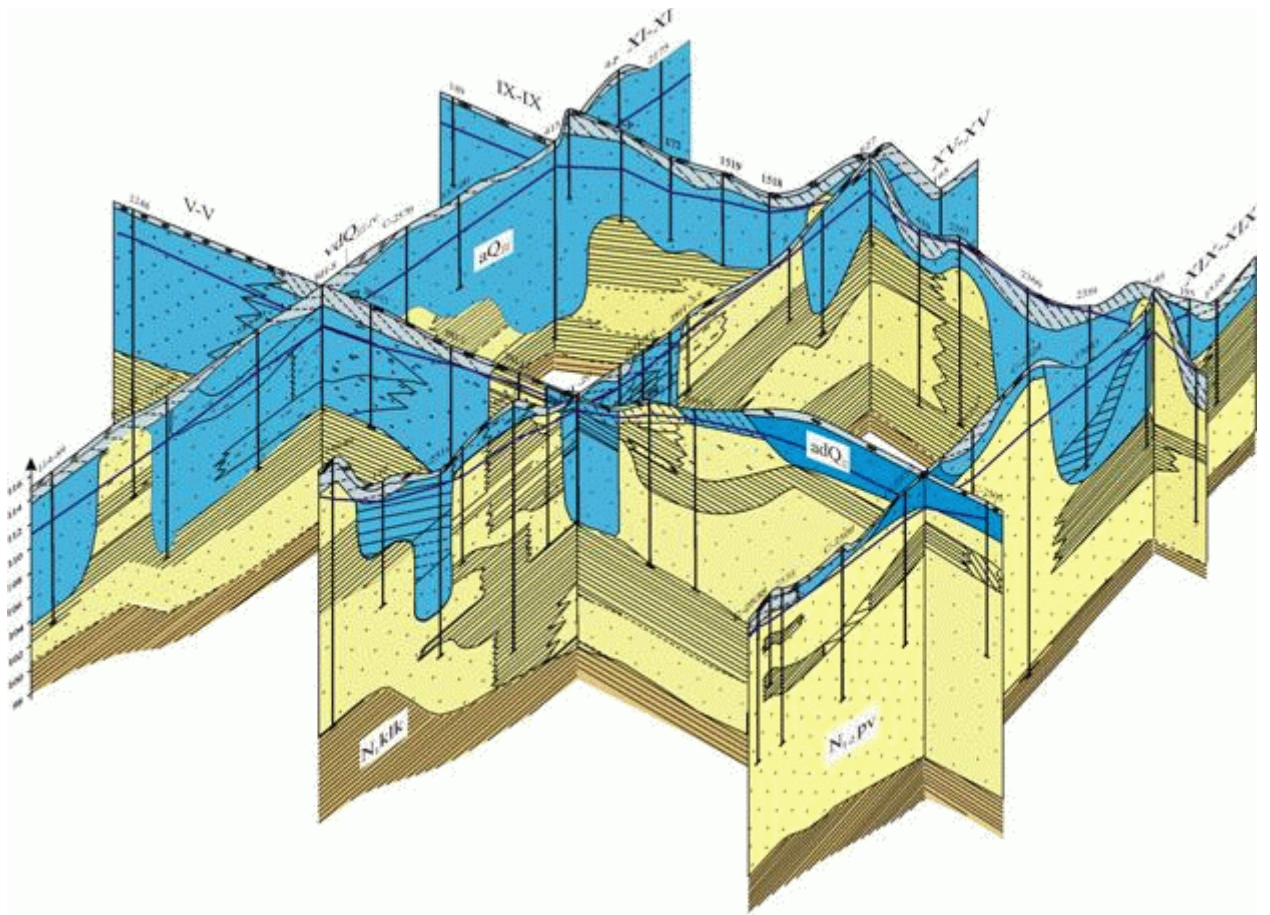


Fig.5. Three-dimensional diagram of lithologic structure of simulated Northern Industrial Area of Pavlodar

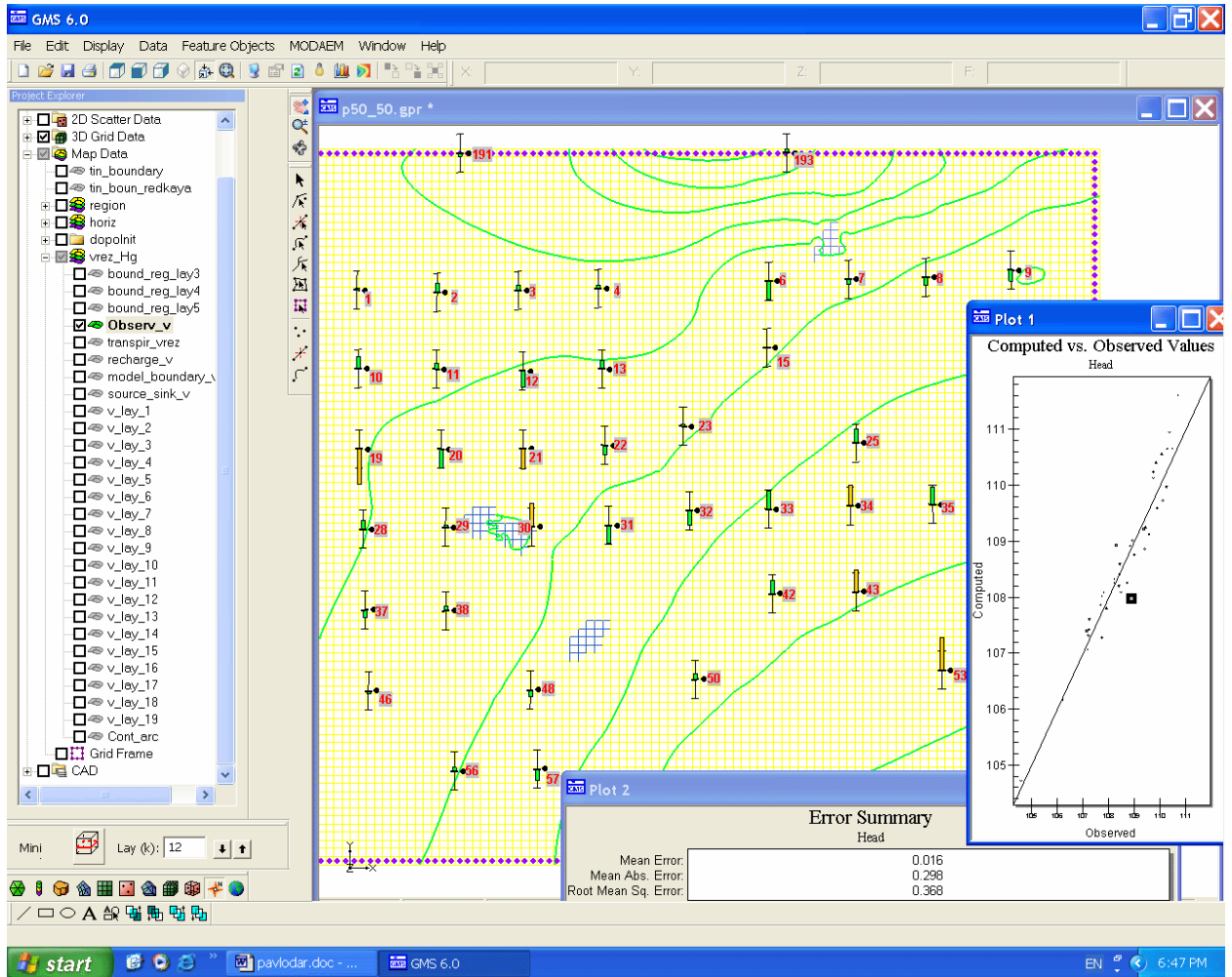


Fig.6. Result of inverse stationary task solution of hydro-dynamic model of Northern Industrial Area of Pavlodar

### **ANNEX 3: Abstracts of papers published for the first year**

**1. P.Randall, M. Ilyushchenko, E. Lapshin, L.Kuzmenko. Case Study: Mercury Pollution Near a Chemical Plant in Northern Kazakhstan. The Magazine for Environmental Managers, N2, 2006, P. 19-24.**

**2. M. Ilyushchenko, P. Randall, T.Tanton, A.Akhmetov, R.I. Kamberov, L.Yakovleva. Activities to contain mercury pollution from entering the river Irtysh in Pavlodar, Kazakhstan. Paper S-285, in: Abstracts of Eighth International Conference on Mercury as a Global Pollutant (Madison, Wisconsin; August 6-11, 2006). DEStech Publication, Inc., 2006.**

The threat of polluting the Irtysh River by mercury was caused by high losses of Hg during 1975-1993 at chlor-alkali production in outskirts of Pavlodar, Kazakhstan. These losses were the highest among similar factories in the former USSR and could be estimated as 1.6 kg Hg per ton of produced caustic soda (total losses of mercury could be estimated as 1310 tons of those 1100 tons were mechanical losses). The majority of metal mercury concentrated beneath electrolysis shop formed the hotspot of groundwater contaminated by soluble mercuric chloride. Also losses of Hg-contaminated wastewater from sewage system, contamination of topsoil and wastewater storage – Lake Balkyldak (having capacity more than 80 million m<sup>3</sup>) took place. The closest sites subject to risk of mercury pollution are village Pavlodarskoye having 200 ha of groundwater fields and the Irtysh River located 3-5 km to the west from chlor-alkali production.

Original design of clean-up was developed in 1995. The scope of designed works included excavation and thermal treatment of highly contaminated materials with purpose to recover marketable metal mercury.

The research carried out during 2001-2005 has shown that the extent of Hg contamination posing the risk for environment and public is much higher than it was thought before. This allowed revision of strategy for the management of mercury contamination in Pavlodar. Instead of expensive and non-effective recovery of Hg from wastes the containment strategy was proposed assuming isolation of major hotspots from atmosphere, surface run-off and groundwater. In 2003-2005 the impermeable clay barrier (cut-off wall) was constructed around four major hotspots. The depth of cut-off wall reached basalt clay at 15-20 m and its width was 0.6 m. The total length of the barrier is 3588 m. Contaminated topsoil was excavated to the depth 0.5 m and removed to the sites isolated by cut-off walls. The hotspots were covered by clay on total area of 180000 m<sup>2</sup>. All buildings contaminated with mercury were demolished and the debris was placed into 3 m deep pit lined with 0.5-m clay layer. These materials were further stabilized with cement and covered with asphalt layer forming the monolith storage with total area 15671 m<sup>2</sup> which is stable against the impact of groundwater and surface runoff.

Since 2005 local authorities initiated 15-year Program of mercury contamination monitoring in Northern industrial area of Pavlodar. This Program is expected to answer the question whether the clean-up activities implemented to date are sufficient. US EPA gives a support to this program via ISTC launching three-year project K-1240 since 2006.

# Press-release

Pavlodar  
July 12 2006

BG KAZAKHSTAN



**Topic: Scientists of BG Chair of Almaty Institute of Power Engineering and Telecommunication (AIPET) together with local authorities assess the results of the implemented “Program of Mercury Decontamination in the North Industrial Zone of Pavlodar”**

## **Press-conference participants:**

**Vladimir Bednenko**, Head of Pavlodar Oblast environmental department

**Nikolai LEONTYEV**, deputy head of Pavlodar Oblast environmental department

**Artur AKHMETOV**, deputy director of Pavlodar Chemical Plant, manager of Demercurization Program

**Mikhail ILYUSHCHENKO**, Leader of international research projects on risk assessment and post-demercuration monitoring in Pavlodar, PhD in Chemistry, associate professor of Environmental Technology Chair BG, AIPET

**Assel IBRAYEVA**, “BG Kazakhstan” PR adviser

**July 12, 2006 – Press-tour to Pavlodar Chemical plant (former JSV «Khimprom»).** Event organizers – scientists of BG Chair on Environmental Technology, AIPET – informed journalists about the results of the 1 Phase of Program of Mercury Decontamination in the North Industrial Zone of Pavlodar. Mass media representatives were introduced to the results of implemented activities and research projects on environmental assessment and risk reduction posed by mercury contamination. They were presented with a Program of post-demercuration monitoring up to 2020.

Main purposes of the Program of post-demercuration monitoring in the North industrial zone are (i) to determine the level of mercury accumulated in the environment (air, soil, surface and underground water) after the Program of mercury decontamination of chlor-alkali industry, (ii) control for 15 years the change of this level, and (iii) affirmation of risk absence for population health.

Results of proposed demercurization program shall prove the efficiency of demercurization activity of 2001 – 2004.

In case contamination residue declines up to acceptable risk level Program of mercury monitoring can be accomplished by 2020.

In case of risk growth due to the increase of mercury concentration in soil, air, underground and surface water any Phase of the Program will be a subject to amendments and additional rehabilitation activities.

**Mikhail ILYUSHCHENKO**, Leader of international research projects on risk assessment and post-demercuration monitoring in Pavlodar reported: *«Accomplishment of the Phase 1 of Demercurization project became feasible because of the right assessment of the problem*

*importance by President, National and local Governments, their support, well organized work of scientists and engineers from Kazakhstan, Ukraine and Great Britain. AIPET BG Chair scientists worked out a Program of 15-years mercury monitoring that will assess efficiency of fulfilled demercurization works. Currently there are a number of new and unique technologies being developed by scientists of our Chair and western companies. These technologies will be sufficient enough to reduce the residue risk level in underground and surface water. At present Kazakhstan is the world leader in full scale demercurization activities ever implemented. This attracts the attention of Russian and western scientists since the problem of mercury contamination by industries is one of the most acute problem in the world environment».*

Program of post demercurization monitoring is being implemented for 2 years and funded from the oblast budget. American Government through the ISTC provided additional funding to BG Chair for this Program fulfillment. For this money a new monitoring laboratory shall be created in Pavlodar (in the site of the former JSC “Khimprom”), that will be equipped with the modern analytical devices and staffed with a qualified personnel capable to work on modern methods.

Currently a research expedition of BG Chair scientists scheduled in the Program is working in Pavlodar investigating the current plume of mercury contaminated underground water. Their scope of work covers about 100 boreholes to investigate (including water sampling and its analyses). They use a mobile laboratory facilitated with mercury analyzer made in UK with detection limit of up to 4 ng/l. This value is 100 times lower than Maximal Allowable Concentration for mercury in water. Thus, the analyzer is capable to detect actually traces of mercury in water. This expedition will show whether accomplished measures were sufficient to stop mercury getting in the ground water and how far all unfavorable factors have been considered.

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## **Additional information**

### **History**

Phase 1 of the unique project having confined mercury spread in the North industrial zone in Pavlodar was accomplished in the beginning of 2005. The project has been funded mostly from the National budget which helped to avoid further mercury spreading in particularly towards the Irtysh River and underground water pollution. Project implementation process has been discussed in numerous Kazakhstani – Russia meetings at different levels. While implementing it was revealed that chlor-alkali industry left behind about 1310 tons of metal mercury and mercury compounds. This mercury was accumulating under the floor of Shop №3, has been spread with the winds from the mercury wastes sites and entered surface and underground water. It was a really huge risk for the personnel health and the health of population of Pavlodar suburbs who used underground water in households. In the early stage of demercurization (April 1999) intensive mercury vapor emission was reported that was originated from the semi-demolished building N 31. Due to the thread for city population health the emergency situation was declared.

In Kazakhstan the attention to the mercury pollution was attracted by local administration, NGOs and local mass media. Pavlodar inherited the problem from the former Soviet Union and nobody in Kazakhstan wanted to take responsibility for this contamination and hid the real danger. The main problem in the years of economic and political crisis was to find funding to investigate the scale of contamination and risk, develop and implement demercurization technology. Prompt

and first steps to cope the problems were undertaken at the cost of plant own money and the Pavlodar oblast budget. These works were initiated by Danial Akhmetov – Head of oblast administration, who currently is a Prime-Minister of the Republic of Kazakhstan.

Top priority measures included the collection of necessary data and materials for projecting, as well as the demercurization project development and dismantling of the main source of contamination - electrolysis shop No.31. This work was being done in 1993-1999. Ukrainian Institute JV “Evrohim”- Kiev (JV Evrohim) held engineering investigation and developed the project of shop 31 demercurization. Plant workers have collected 17 tones of metallic mercury and 3 tons were extracted after the thermal treatment of construction materials. Materials of central part of the shop 31 which contained less 0,3% mercury were put in burial ground, construction of which was started at industrial site of chemical plant in 50 meters from the dismantled shop. Such disposition of burial ground has prevented the spread of original hotbed.

In 2000 all works at the area of Pavlodar Chemical Plant have been stopped due to the lack of funding. The Government of the Republic of Kazakhstan did its best to attract investments or loans from foreign companies for demercurization works. Starting from 1993 RK President N. Nazarbayev had meeting with Japan Government discussing participation of Japanese companies in mercury contamination remove and construction of new chlorine production in Pavlodar with no-mercury method. In 2000 N. Nazarbayev had similar meetings in France where he signed Agreement on soft loan to be received from France Government. This soft loan had to help in rehabilitation of contaminated site and in collaboration with French companies, which offered technical assistance and participation in all demercurization works. However this negotiation was overextended and eventually ended in no results. French company BRGM assigned by French Government refused to hold demercurization without protracted and expensive preliminary study.

In 2001 Consortium of Kazakhstani and European universities with British Gas Chair of Almaty Institute of Power Engineering and Telecommunication as a leading institute received grant of INCO–Copernicus [www.nip.kz](http://www.nip.kz), <http://ccip.csa.ru/uch10.htm/> and held two years research of mercury impact on environment in Pavlodar. This research showed there are several secondary centers of contamination on the site beside the main one. Mercury was washed out of these centers and formed plume of underground water contaminated with mercury dissolvable salts and spread in narrow line of 2,5 km towards north along the Irtysh River. Forecast of plume behavior made on the base of computer model by Institute of Hydrogeology and Hydrophysics showed that with the change of hydrogeological scenarios can result in change of this plume direction and bring it to Pavlodarskoye village and the Irtysh River. It made scientists revise the original project of mercury pollution center abandonment. Instead of extraction and treatment of metallic mercury from concrete basement of shop 31 and soil underneath it was suggested that main pollution centers had to be isolated from underground water and ambient air contact. Original project implementation required much funding with no effect guaranteed because it was impossible to extract all mercury and to sell it. Scientists suggested that mercury had to remain in its location and to be isolated with cut-off wall, which had to be constructed with converted heavy machinery. This idea was considered at the meeting of Kazakhstani National Academy of Science and was recommended as an amendment to demercurization project.

JV Evrohim reacted immediately and amended Work Program of Demercurization project (since JV Evrohim was a participant of INCO – Copernicus research project). During the second stage of the Demercurization Program in 2001-2004 hotbeds have been confined. Building and construction involved in the production process were dismantled. The most contaminated soil was removed up to the depth of 1 m and the burial site for solid mercury wastes of 0.3-1.0% was constructed.

Demercurization Program could eliminate the risk of environmental pollution and stop the mercury enter the water. According to scientists it will secure the gradual self-cleaning of surface water. Industrial site of the former JSC “Khimprom” is still located on mercury contaminated soils but the spread of mercury is expected to stop.

At the moment a new biotechnology is under development that pertains to underground water cleaning. It is being developed by efforts of Institute of microbiology and virology and AIPET BG Chair. New projects will be funded by US EPA and the pilot tests are scheduled for 2008.

### **BG Chair, Almaty Institute of Power Engineering and Telecommunication**

A key project of BG Group in the field of environmental protection is the creation of chair of environmental technologies at Almaty Institute of Power Engineering and Telecommunication. BG Group provides a sponsor support since 1994, in that way giving an incentive to tackle acute environmental problems in Kazakhstan.

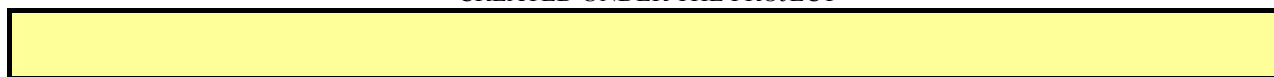
BG Chair is involved in the solution of problems such as water resources management and industrial pollution reduction. In 1996 BG Chair in cooperation with Southampton University organized Master Course at AIPET. This intensive one-year program trains specialists, scientists and managers possessing necessary knowledge and experience in the field of environmental protection. For the first decade BG Kazakhstan invested in BG Chair 1.8 million USD.



## ANNEX 4: Information on patents and property rights.

Annex to quarterly technical report  
on execution of the ISTC project K-1240p  
for the period 1.07.06-30.09.06

ACTIVITIES ON IDENTIFICATION, PROTECTION AND EXPLOITATION OF INTELLECTUAL PROPERTY  
CREATED UNDER THE PROJECT



<b>E V E N T S</b>	<b>Yes</b>	<b>No</b>
Non Disclosure Agreement (NDA) has been signed (with collaborator or with other persons or organizations)		<b>No</b>
New solution (below called "innovation solution") that could be considered as an object of Intellectual Property has been identified (created, obtained)		<b>No</b>
Notification on identification of innovation solution has been submitted to the ISTC		<b>No</b>
Formal description of innovation solution has been submitted to the ISTC		<b>No</b>
Solution to protect innovation in a form of commercial secret has been taken		<b>No</b>
Application for registration of software / Data Base / IC Topography has been submitted		<b>No</b>
Application for patent has been filed		<b>No</b>
National		<b>No</b>
Eurasian		<b>No</b>
PCT		<b>No</b>
Application for patent in the territory of other country has been filed		<b>No</b>
Patent has been obtained		<b>No</b>
National		<b>No</b>
Eurasian		<b>No</b>
other countries		<b>No</b>
Registration of software / Data Base / IC Topography has been confirmed		<b>No</b>
Formal request for licensing / technology transfer has been received		<b>No</b>
Negotiation on licensing / technology transfer has been formally initiated		<b>No</b>
Agreement on licensing / technology transfer has been signed		<b>No</b>
Agreement on licensing / technology transfer has been registered		<b>No</b>
Request for patenting financial support has been submitted to the ISTC		<b>No</b>
Request for patenting consulting support has been submitted to the ISTC		<b>No</b>

Project manager

A handwritten signature in black ink, appearing to read 'M. Ilyushchenko', written in a cursive style.

M.Ilyushchenko