

## **Technical Report**

### **Project 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 Industrial Area of Pavlodar”

For fourth quarter (July-September 2006)

**(Tasks 1-5)**

**Leading Institute:**

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

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### 3. Brief description of the performed work:

The objectives of the work for the reported period are: (i) field works on sampling and measurements carrying out at the area of mercury contamination in Pavlodar, (ii) chemical analytical works in the laboratory of Almaty Institute of Power Engineering and Telecommunications (AIPET), (iii) data processing, creation of database and cartographic materials based on the results of mercury monitoring of 2006, (iv) production of a local model of the area of groundwater mercury contamination with help of GIS 6.0 software, (v) preparation of documents for arrangement of monitoring on the storage pond – Lake Balkyldak for Regional Environmental Protection Authority of Pavlodar oblast, (vi) presentation of the results of monitoring at Regional Environmental Protection Authority of Pavlodar oblast, mass media, scientific journals and conference.

## I. Field works

### 1.1. AIPET

In fourth quarter AIPET implemented field works in Pavlodar in July and September.

#### 1.1.1. Summer field works

Summer field works were started in the third quarter having proceeded with monitoring of groundwater, soil and air in July.

##### 1.1.1.1. Groundwater sampling

Groundwater samples were being taken from 107 observation boreholes of the system of mercury monitoring at Northern industrial area of Pavlodar using a submerged electrical pump for two months (June and July) according to the technique developed by AIPET in 2001-2002 and based on very careful rinsing of equipment for borehole pumping and on sampling quality control (fig. 1-5).

Water samples were taken in duplicate into single-use plastic bottles and preserved by concentrated hydrochloric acid at the sampling place. Coca-cola plastic bottles of 0.5 liter purchased in a grocery shop were used. Before 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, filled with groundwater up to the mark and then 2.5 ml of the preservative were added there. After that the bottles filled with groundwater samples were screw-topped and enclosed within plastic bags



Fig. 1. Groundwater pumping out of an observation borehole, pH Measurement



Fig. 2. Groundwater pumping out of an observation borehole



Fig. 3. Groundwater pumping out of an observation borehole



Fig. 4. Equipment rinsing after groundwater sampling



Fig. 5. Equipment rinsing after groundwater sampling

(the same procedures were done for bottles with both rinsing water and blank samples, except that the bottles with blank samples were filled with distilled water beforehand in the laboratory and the preservative was added into this bottles only in field conditions). 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) and also in every day analysis of two blank samples. All water samples and blanks were delivered to the chemical analytical laboratory at the day of sampling.



### 1.1.1.2. Soil sampling

19 soil samples were taken at the industrial area of the former chlor-alkali production and around it in order to estimate efficiency of demercurisation works performed in 2002-2004. 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) (fig. 6) 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  $45^\circ$ , 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.



Fig.6. Soil sampling

### 1.1.1.3. Measurement of mercury vapors in the air

Also efficiency of demercurisation works was estimated with help of analysis of the near-earth layer of the air (10 cm of ground surface) for mercury vapors content. The measurements were implemented in cooperation with specialists from AO GEOTestBRNO (Brno, Czechia) (fig. 7-9) using portable mercury atomic absorptive spectrophotometer (AAS) Lyumex RA 915+ (Russia) according to the method of the instrument manufacturer.

Results of measurements of mercury vapors concentration at near-earth layer of atmosphere carried out since 3 pm till 6 pm on the 21<sup>st</sup> of July, 2006 at the air temperature of  $27^\circ\text{C}$  ("Summery table 02.2006") were in following limits: about

200 ng/m<sup>3</sup> (2 measuring points) – in the centre of landfill for building structures (50 m to the south from the former building 31) (fig. 10), from 100 to 17000 ng/m<sup>3</sup> (12 measuring points) – at the industrial area of the former chlor-alkali production around the buildings 31 and 34, from 100 to 200 ng/m<sup>3</sup> (4 measuring points) – at the place of special ponds for solid and liquid mercury wastes located on the south shore of wastewater storage pond Balkyldak, 900 ng/m<sup>3</sup> (1 measuring points) – in site of 6<sup>th</sup> wastewater pumping station. There are two sanitary norms for mercury vapors content in the air: maximum permissible concentration in working are, MPC<sub>wa</sub> – 10000 ng/m<sup>3</sup> and maximum permissible average daily concentration in atmosphere, MPC<sub>ad</sub> - 300 ng/m<sup>3</sup>.

The results of measurement of mercury vapors concentration at the place of the special ponds for mercury wastes (fig. 9) and above the covering of landfill for building structures (fig. 10) say about quite good containment of the mercury wastes. For the industrial area of the former chlor-alkali production and former 6<sup>th</sup> wastewater pumping station high (in excess of MPC<sub>ad</sub>) mercury vapors concentrations (5 measuring points) were measured at places not covered with clay screen and extremely high (in excess of MPC<sub>wa</sub>) mercury vapors concentrations (1 measuring point) – at the place of the clay screen washing away by atmosphere precipitation above the concrete foundation of the building 31 (fig.7).



Fig. 7. Measurement of mercury vapors concentration in the near-earth air at the industrial area of chlor-alkali production (in site of the building 31)



Fig. 8. Measurement of mercury vapors concentration in the near-earth air at the industrial area of the chlor-alkali production (in site of the building 31)



Fig. 9. Measurement of mercury vapors concentration in the near-earth air at the place of special ponds for solid and liquid mercury wastes





Fig. 10. Landfill for mercury containing building structures located 50 m to the south from the former building 31

#### **1.1.1.4. Measurements of groundwater tables**

In July AIPET together with IHH were being carried out the measurements of groundwater tables in 239 observation boreholes for 5 days. The measurements have been done 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. IHH used the results of these seasonal measurements (“Summery table 03.2006”) to create the local model of groundwater mercury contamination.

#### **1.1.2. Autumn field works**

##### **1.1.2.1. Measurements of groundwater tables**

Measurements of groundwater tables in 230 observation boreholes were being carried out for 7 days. The results of seasonal measurements (“Summery table 04.2006”) were delivered to IHH for their use in the local model of groundwater mercury contamination.

##### **1.1.2.2. Soil sampling**

111 soil samples were taken in the five points of possible pinch of mercury contaminated groundwater on regular grid according to previously prepared sam-

pling plan. The samples were taken from topsoil (0-10 cm) (the sampling points were coordinated using portable GPS) into duple plastic bags, tagged and sent to AIPET Laboratory in Almaty.

### **1.1.2.3. Topographical survey of outline of impervious barrier so called “cut-off wall”**

Together with Mr. A. Akhmetov (manager of demercuration works of 2002-2004) coordinating cut-off wall around the main hot spot of mercury contamination under the former building 31 was carried out using portable GPS. The results were used for development of GIS of mercury pollution in Northern industrial area of Pavlodar created in 2001-2002.

### **1.1.2.4. Development of the method of finding distribution border of underground hot spot of oil products pollution**

Depth of upper boundary surface of underground contaminating spot of oil products and its spread to the west were investigated near the western fence wall of industrial area of Pavlodar Oil Refinery (POR) at the distance of 500 m from its western corner.



Fig. 11. Drilling of the first test borehole to study spread of oil products pollution near the industrial area of Pavlodfar Oil Refinery



Fig. 12. Drilling of the first test borehole to study spread of oil products pollution near the industrial area of Pavlodfar Oil Refinery

For that 4 boreholes 5.5 m deep 10 m far from each other were drilled on the profile of sub-latitudinal direction using a hand drill (fig. 11). The first borehole (fig. 12) was 3 m far from observation hydro-geological borehole #54 (located 5 m far from the fence wall of POR) where groundwater oil products pollution had been found before (2001-2002) (fig. 13). During field works groundwater table in the observation borehole was found to be 5.20 m. At drilling the first and the second boreholes strong smell of oil products appeared starting from the depth of 4 m from the ground surface that was an evidence of the presence of contamination there. There were not found oil products in the third and fourth boreholes. Thus at present spot of oil products pollution has spread 25-30 m to the west from industrial area of POR and had thickness not less than 1 m.

## 1.2. Pavlodar State University (PSU)

### 1.2.1. Sampling of bottom sediments of wastewater storage pond Balkyldak

Together with AIPET 33 samples of bottom sediments of wastewater storage pond Balkyldak (fig. 14-15) were taken from a boat board from 17 sampling points according to "Sampling plan for 200 sampling points" (fig.1 from Technical report on K-1240 project for II quarter) located near the shore and therefore inaccessible for sampling in winter time (near the shore water freezes through down to the bottom). Samples of bottom sediments were taken using samplers of two different constructions: soft sediments (if available) were taken layer by layer with interval of 50 cm; clays sediments (including clays underly



Fig. 13. Oil products pollution in observation borehole # 54



Fig. 14. Equipment for bottom sediments sampling





Fig. 15. Off-shore sampling of bottom sediments on wastewater storage pond Balkyldak

ing soft sediments) were taken only from the surface layer down to 25 cm deep (sands were not taken). Coordinates of sampling points were found with help of portable GPS with maximum error of 7 m. At the same time bathymetric measurements and measurements of soft sediments thickness were carried out ("Summary table 01.2006). Bottom sediments samples were put into tagged duplex plastic bags. After each sampling the equipment was being cleaned very carefully from caught-on sediments and water (there was no cleaning quality control). The samples were frozen and delivered to AIPET Laboratory in Almaty where were stored in frozen state.

### **1.2.2. 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 (fig. 16-26). 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); mollusca, benthos and plankton – 1, 4 and 2 samples respectively both for 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



Fig. 16. Morphological measurements of fish caught out of wastewater storage pond Balkyldak



Fig. 17. Determination of age of fish caught out of wastewater storage pond Balkyldak



Fig. 18. Plankton sampling in wastewater storage pond Balkyldak



Fig. 19. Plankton sampling



Fig. 20. Sampling of water insects



Fig. 21. Benthos sampling





Fig. 22. Benthos sampling



Fig. 23. Molluscs collecting

which were taken on the shore and rinsed many times at the sample stations. Species belonging was not determined. Molluscs 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 August 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 – at the cost of Irtysh River floods, ichthyo-fauna consists of crucian, roach, pike and perch).

In current year in spring-summer time more than 30 students were attracted as educational training to research biota of pond Balkyldak. In 2005/2006 academic year two diploma works and one master course dissertation of G.A. Arynov were defended on the problem of pond Balkyldak mercury contamination. In 2006/2007 year three diploma works are being gone up on this problem.

## **II. Chemical analytical works**

AIPET team carried out groundwater analysis for total mercury content in the laboratory building provided by AO “Kaustik” at the territory of former “Khimprom”, Pavlodar using equipment delivered from Almaty. The rest chemical analytical works were done in AIPET Laboratory in Almaty. All operations on samples preparation and their analysis for mercury content were being conducted using minimum of laboratory glassware (one-use if possible) 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”. Quality control 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.

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 whereupon 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 muriate 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 mercury determination in soils and bottom sediments** 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 muriate 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).

The results of analysis were used to create a database ("Summary table 05.2006, Summary table 06.2006 and Summary table 07.2006).

### III. Office studies

Electronic summary tables which formed the database of post-demercuration monitoring were compiled by AIPET team on the results of field study and chemical analytical works.

The results of mercury concentration determination in groundwater at the area of mercury pollution (“Summary table 05.2006) were inserted on the vector map together with the results of similar research of 2004 and 2005 (fig.27, Table 1). This allowed 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 with cut-off wall).

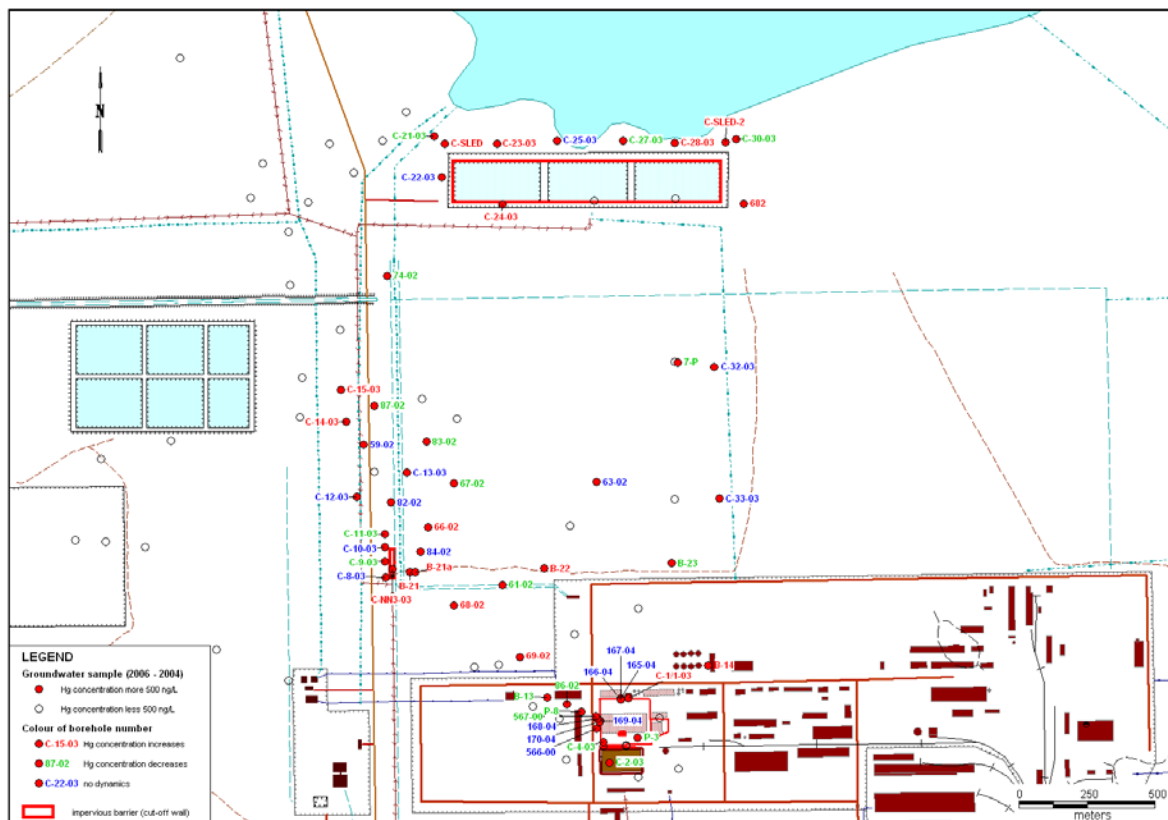


Fig. 27. Map-scheme of location of observation hydro-geological boreholes of mercury monitoring system at Northern industrial area of Pavlodar



Table 1

Change of total mercury concentration in groundwater of Northern industrial area of Pavlodar (according to 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	C-21-03	4425		1630
7	C-SLED	3195		not able to pump
8	C-22-03	1400		1200
9	C-24-03	2995		not able to pump
10	C-26-03	19		not able to pump
11	C-29-03	58		not able to pump
12	C-30-03	45250		23500
13	C-SLED-2	90650		not able to pump
14	C-28-03	5390		not able to pump
15	C-23-03	648		not able to pump
16	C-25-03	2455		2180
17	C-27-03	24450		12500
18	C-15-03	1625		11800
19	C-14-03	2875		7450
20	C-13-03	6175		4700
21	C-11-03	29550		16400
22	C-12-03	28850		31500
23	C-8-03	35400		43500
24	C-9-03	27200		17600
25	C-NN3-03	6025		not able to pump
26	C-34-03	80		86
27	C-35-03	171		737
28	C-33-03	943		941
29	C-32-03	43850		40600
30	63-02	5050		3950
31	62-02	35		21
32	C-6-03	21		138
33	84-02	28850		30800
34	67-02	854		493
35	83-02	798		493
36	72-02	69		44
37	90-02	140		140
38	74-02	1435		338
39	87-02	9315		6150
40	70-02	105		307
41	73-02	479		744
42	79-02	126		919
43	55-02	50		59

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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		10500
89	<b>166-04</b>	not observed		3380
90	<b>167-04</b>	not observed		3310
91	<b>169-04</b>	not observed		28200
92	<b>170-04</b>	not observed		6880
93	<b>168-04</b>	not observed		7220
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).

The results of determination of mercury concentration in bottom sediment samples (“Summary table 06.2006) 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 (this work is being carried out now). Final map and calculation of amount of mercury in sediments will be produced after sampling and analysis of bottom sediment samples according to “Sampling plan for 200 points” (fig. 1 from Technical Report on K-1240 project for II Quarter).

The results of determination of mercury concentration in soil samples taken at the industrial area of former chlor-alkali production maximum of which could be in the order of g per kg (“Summary table 07.2006) together with the results of measurement of mercury vapors concentration in near-earth layer of the atmosphere maximum of which could be in the order of tens of thousands of ng per m<sup>3</sup> (“Summary table 02.2006) suggest high-level risk still remaining for working staff and also insufficiency of clean up measures performed at the territory of former PO “Khimprom”, Pavlodar according to the Program of demercurisation of 2004-2004. This necessitates conducting more detail investigation of topsoil mercury contamination at the industrial area of the plant in the framework of K-1240 project resulting in production of new map of the contamination.

#### **IV. Simulation of groundwater mercury contamination**

IHH continues the work to improve their model of groundwater mercury contamination.

**Completion of formation of local model informational database.** Based on produced detailed hydro-geological cross sections the model boundaries and its grid approximation have been made more precise. Simulated area was presented in horizontal projection as a rectangle with the area of about 18.0 km<sup>2</sup>. In section it was schematized as 19 layers. In horizontal projection the simulated area was approximated with orthogonal grid with step of 40 m and block size of 113 x 92. Outer boundaries of the detailed local model were schematized by the type 1 boundary conditions. Groundwater heads established on outer boundaries of the local model changing with time will correspond to groundwater heads obtained on the regional model of the northern part of Pavlodar industrial area. Maps of hydro-geological parameters have been produced for each of 19 layers of the local model and then were represented as three-dimensional grid.

**Model calibration.** 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.

Inverse non stationary task is being solved at present. Change of hydro-geological conditions since 1970 till 2001 is being reproduced in the model. Coefficients of both elastic and gravitational water loss of bearing strata are being adjusted; groundwater recharge coming from losses of technical water from engineering services is being made more precise.

Prognosis tasks definition will be specified after the model calibration completion and their solving will be started.

## **V. Interaction with regional authority.**

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 Akim and Office of Public Prosecutor of Pavlodar oblast. Permanent and most important subject of the discussion was prevention of fishing from the mercury contaminated wastewater storage pond – Lake Balkyldak that poses a threat to Pavlodar population health.

Also “Science based recommendations on arrangement of wastewater storage pond Balkyldak monitoring” and “Research Program of wastewater storage pond Balkyldak” have been developed on the instruction of Pavlodar Oblast Akimat in order to make decision on further safe use of the lake (see Annexes).



## VI. Presentation of obtained results

Scientific results of the monitoring works of 2006 were presented (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 August, 2006), ISTC in (iv) Oxford, UK (20-26 August, 2006) and (v) Almaty (19-20 September, 2006), published as proceedings of International Conference /1/ and the article in USA scientific journal /2/.

AIPET, BG Chair of Environmental Technology has arranged press-tour to inform public of Kazakhstan with the results of the first stage of Demercurisation 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 (see press-release in Annexes). Vladimir Bednenko a head of Pavlodar Territorial Environmental Protection Authority, Wilhelm Franz a competitive manager of AO “Pavlodar Chemical Plant” and Mikhail Ilyushchenko a manager of ISTC K-1240 project addressed the press-conference. 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 were located on 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/.

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.

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 color. **Kazakhstanskaya Pravda**, 11 August, 2006.
4. Realization of the Program of Mercury Monitoring 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.

#### 4. Executed stages:

Task 1, stage 1-3 - partly,  
 Task 2, stage 1 - completed, stage 2, 3 - partly,  
 Task 3, stage 1, 4 - partly,  
 Task 4, stage 1 – completed, stage 2-5 – partly,  
 Task 5, stage 1, 2 - partly.

#### 5. Important business trip:

From K-1240 project budget: two business trips for AIPET to USD to participate at Eighth International Conference “Mercury as a Global Pollutant” (Madison, Wisconsin, USD, 6-11 of August 2006) and several business trips for AIPET from Almaty to Pavlodar to carry out field works in the area of mercury pollution.

From other funding sources: two business trips for AIPET to Prague to participate at “BIOMERCURY” project Workshop, Czech Republic (18-19 of May 2006), one business trip for AIPET to participate at 29 AMOP Technical Workshop (Vancouver, Canada, 6-8 June ), 7 business trips for AIPET, IHH, PCP, PSU (accordingly – 2, 2, 2 and 1) to Oxford, United Kingdom (20-26 August 2006) to participate at ISTC Workshop, 2 business trips for PCP to USD to participate at Eighth International Conference “Mercury as a Global Pollutant” (Madison, Wisconsin, USD, 6-11 August 2006) and several business trips for

AIPET from Almaty to Pavlodar to arrange seminars and meetings with local authority.

#### 6. Main acquired equipment:

In forth quarter expensive equipment was not acquired because funds scheduled for their purchase have not been transferred from PCP to AIPET until now.

#### 8. Current state of affairs:

Work is going on reduced work plan because of absence of JSC PCP as key Pavlodar partner. AIPET has committed the most part of PCP work. In fact current year Stepnogorsk partner BMP has not started working on the project because of their internal organizational difficulties.

#### 9. Delays, problems, suggestions:

PSU together with AIPET had been able to organize fulfillment of a part of field work on Lake Balkyldak by the end of summer field season, including involvement of students. All work scheduled for 2006, which have not been fulfilled yet is intended to be done during field season of 2007.

There has been no progress yet in change of JSC PCP Pavlodar partner for JSC “Kaustik”, that has not allowed proceeding to main objective of K-1240 project: organization of monitoring laboratory in Pavlodar, which would give an opportunity to weapon - scientists of former JSC “Khimprom” to participate in ISTC programs.

The fact that Stepnogorsk partner BMP has been in state of reorganization for whole year discredits the possibility to implement the part of K-1240 project Work Plan related to monitoring of groundwater pollution with oil products (in order to carry out this it is necessarily to purchase expensive chemical-analytical equipment, to train personnel of Pavlodar laboratory to work on it, to carry out first monitoring and then to drill sufficient number of observation boreholes to study distribution of the plume of groundwater contaminated with oil products).

Besides administration of Pavlodar Oil Refinery has not shown their interest in cooperation with K-1240 project team, without which such work becomes inexpedient at all.

At the same time during the discussion of K-1240 project plans at Workshop in Oxford, UK (20-26 August, 2006) it was recommended (by British scientists, including professor Trevor Tanton, collaborator of the project) to conduct methyl mercury monitoring in Northern industrial area of Pavlodar, which is more toxic and hazardous form of mercury pollution of water bodies (both surface water and groundwater).

There has been no one chemical-analytical laboratory in Kazakhstan which has had capability to determine organic form of mercury in natural samples.

From our point of view these three points are sufficient ground **to suggest doing correction of K-1240 project Work Plan in order to replace most part of tasks on oil products monitoring by methyl mercury monitoring including the project correction of both budget and list of purchased equipment in 5-th quarter.**

**Also it is necessary to provide K-1240 project Work Plan for correction including more detailed investigation of mercury contaminated topsoil and near-earth layer of atmosphere at the industrial area of Former PO “Khimprom”, Pavlodar.**

K-1240 project manager

M.A.Ilyushchenko



## **A N N E X E S**

## Monitoring of wastewater storage pond “Balkyldak”.

### Background

#### Contents

1. Concept
2. Objectives
3. Monitoring sites and data interpretation
4. Field work and specific monitoring measurements
5. Periodicity
6. Methods of measurements, sampling and analyses
7. Resources and funding

#### 1. Concept

Wastewater storage pond is located in the North Industrial Zone of Pavlodar city in 2 km northward of Pavlodar Chemical Plant and in 5 km eastward of the Irtysh river flood plain (water level in the river in the pond section-line is 104.2 m). Since 1960 it takes industrial, storm sewage, drainage and snow melted water from industries located in this area including Power Plant 2 and Power Plant 3, tractor-building plant, paperboard plant, PCP and oil refinery.

In early 70s the settling pond was handed over to Pavlodar Chemical Plant and by the early 80s the waste water discharges from other industries was ceased (except storm sewage, snow melted and drainage water). To reduce the territory of swamping and negative impact on environment in 80-90 PCP has constructed west and east dyke-dams and clay antifiltration screen “cut-off wall” in west, north and east sites.

Design capacity of the pond was 59.8 mio. m<sup>3</sup>, surface of water mirror – 22.8 m<sup>2</sup> at level of 109.0 m. Maximal water level (110.95 m) was reported on 18.05.1994. After the stop of PCP production water level slightly lowered and fluctuates lightly during season changes (snow melted water and evaporation) at the mark of 110.0 m (11.05.2000 – 110.18 m, 13.09.2002 – 109.85 m). Main source of pond and other water bodies charge is groundwater from Power Plants joint ash lagoon.

Since the settling pond for 20 years took poorly treated (and mostly not treated) waste water of the whole northern industrial area of Pavlodar it had accumulated much toxic compounds including non-ferrous and heavy metals used in galvanic productions, mercury (rough estimate – about 10 tons), petroleum products, technical oils, detergents, solvents, organic compounds (in particular phosphorus bearing), persistent organic pollutants and inorganic salts. After the stop of main waste water discharge from PCP for 10 years the surface water of the pond was self clarified while toxic compounds lay down on the pond bottom. Total mercury concentration in the surface water dropped till 0.1 mg/l (0.5 MPC<sub>w</sub>) and fluctuates at this level depending on the waves that spread man made bottom sediments in the shallow water.

Pond's embankments are overgrown with reed and in clarified water there are much nonpredatory fish founded mainly *Silver Crucian*. Biota immobilizes heavy metals and persistent

organic pollutants in the bottom sediments accumulating them in food chains. Thus most fish species contain mercury of dangerous concentration (0.3 – 1.5 mg/kg (1-5 MPC<sub>f</sub>)). The settling pond “Balkyldak” is a nesting and food lake for migratory birds, as well as the recreation area for commercial and amateur fishing.

The following risks should be taken in account:

1. risk for population because of contaminated fish can be sold in the market,
2. risk for wild life because of food chains accumulating mercury, other heavy metals and persistent organic pollutants,
3. risk for depressions flooding because of high level of water in the pond, during the spring floods or recommencement of PCP,
4. risk for the Irtysh river because of pond’s surface water filtration through hydraulic works and/or water resistant layer which is natural bed of the pond.

Thus monitoring of “Balkyldak” lake should include the following components:

- 1.1. Control of water level in the pond;
- 1.2. Control of contaminated with total mercury groundwater (exceeding MPC<sub>w</sub> = 500 ng/l for dissolved inorganic mercury) moving northward and towards the Irtysh river beyond the hydraulic works;
- 1.3. Control of fishing, especially commercial;
- 1.4. Control of surface water level in the pond;
- 1.5. Monitoring of total mercury and other toxic compounds concentration in the pond fish;
- 1.6. Monitoring of total mercury and other toxic compounds concentration in the pond surface water;
- 1.7. Monitoring of total mercury and other toxic compounds concentration in the pond bottom sediments;
- 1.8. Monitoring of total mercury and other toxic compounds concentration in the pond biota.

## 2. Objectives

Main idea of settler monitoring is to control the safeness of population and environment which can be influenced by the pond. It includes study of surface and groundwater interaction, control of prohibition for fishing as well as determination of mercury and other toxic compounds concentration in the surface water, bottom sediments, fish tissue and other biota elements.

To achieve these aims it is important to solve the following tasks:

- 2.1. determine the order and periodicity of water level measurement both for surface and groundwater in the settler;
- 2.2. determine the order, periodicity and methods of samplings of surface and groundwater to find the concentration of total mercury and other specific pollutants;
- 2.3. determine the order and periodicity of other field work and measurements;
- 2.4. determine the methods of chemical analyses for total mercury determination in the samplings and order of laboratory analyses;

- 2.5. develop recommendation on results interpretation;
- 2.6. determine resources needed for mercury monitoring

### **3. Monitoring sites and data interpretation**

Monitoring should include the water level control in the pond, both sampling and chemical analyses of mercury, other heavy metals and persistent organic pollutants in the samples of surface and groundwater as well as in fish tissue and other biota elements. . List and input data on heavy metals and persistent organic pollutants concentration specific for this pond should be determined with separate study. To sample groundwater it is possible to use the existing boreholes grid with preliminary check of its reliability. Monitoring of the pond should take place in the same most contaminated sites in the south-west part (see the scheme attached).

Obtained data will make a unified data base in order one could use it for years to determine the pattern of change and its danger for population and environment. This data base will be the only tool for the development of standard criteria of results interpretation.

### **4. Field work and specific monitoring measurements**

Measurements of water level should be done with the same depth-gauge with preliminary calibration and affixment to existing geodesy grid. The depth-gauge should have protection against unfavorable nature and anthropogenic impacts and be used for long-term period. It should be placed in west dam of the pond, with easy access in every season and weather conditions.

While sampling the temperature and pH level of surface and groundwater should be measured. While groundwater sampling the water level in boreholes should be measured either.

Fish species caught for analyses should be weighted with precise scale to 1 gr. It is important also to identify its age.

### **5. Periodicity**

Periodicity of monitoring should be stipulated with the rate of hydro – geochemical processes and season fluctuation. With no significant waste water discharge three times a year (spring, summer and autumn) is sufficient to control the fluctuation of water level.

During the first year of groundwater monitoring and measurements of pollutants concentration is also recommended to be carried out three times a year (spring, summer, autumn) with the positive air temperature. The same periodicity is supposed to have while measuring pollutants concentration in surface water of the pond. Later in the following years such measurements could be held once a year (summer or spring).



## 6. Methods of measurements, sampling and analyses

Methods of measurements, sampling and analyses have to be standardized and metrologically certified. Due to low concentration of highly toxic pollutants the methods of sampling and analyses should provide specific procedures for quality control and blanks. Should such methods are not certified in Kazakhstan methods cadastre one uses methods recommended by US EPA.

## 7. Resources and funding

Program of monitoring should have a stable source of funding due to the high risk posed by the pond. Initially it could be funded by the republican budget, oblast budget or oblast environmental fund. Later the funding could be provided by the entity operating this settling pond.

Laboratory staff dealing with sampling and chemical analyses should consist of 4 specialists including the driver/mechanic and team leader.

Computation of funding required for this activity will be done on the base of estimate attached.

08.09.06.

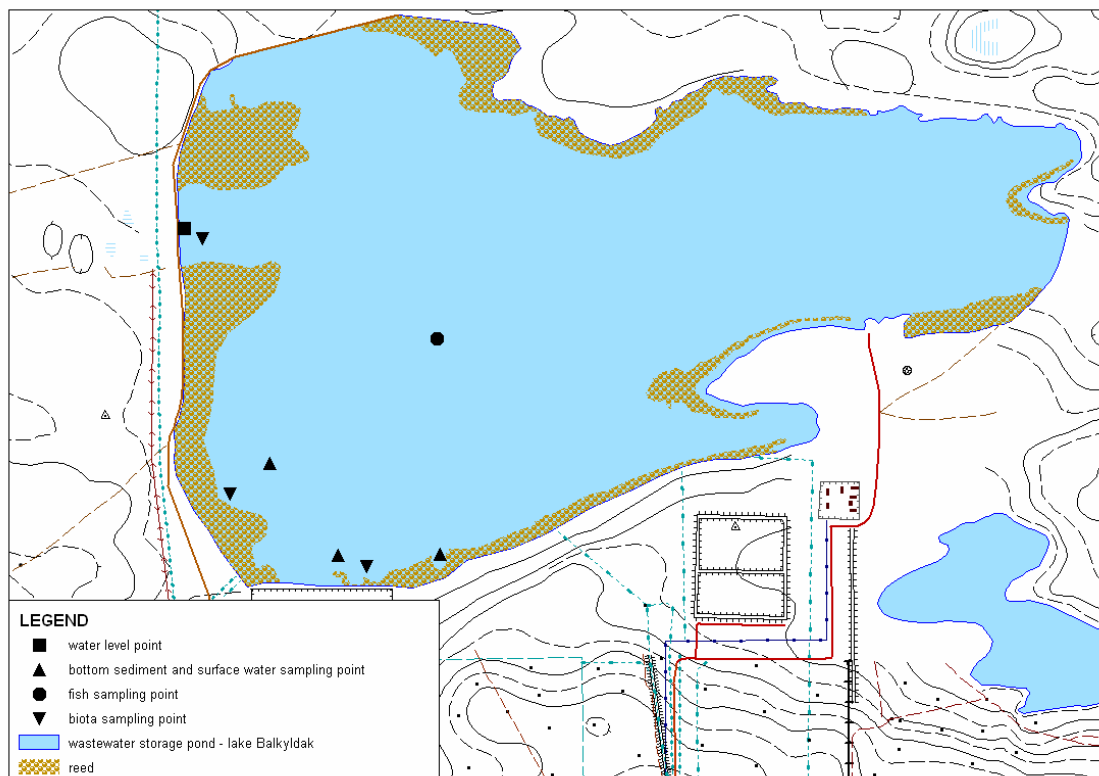


Fig .2. Sampling points (stations) for wastewater storage pond – Lake Balkyldak

## Waste water storage pond Balkyldak. Programm of research

### Background

For 45 years waste water storage pond of PCP, Lake Balkyldak, took industrial, storm sewage, drainage and snow melted water from industries located in the North Industrial Area. It took poorly treated (and mostly not treated) waste water of the whole northern industrial area of Pavlodar it had accumulated much toxic compounds including non-ferrous and heavy metals used in galvanic productions, mercury (rough estimate – about 10 tons), petroleum products, technical oils, detergents, solvents, organic compounds (in particular phosphorus bearing), persistent organic pollutants and inorganic salts. After the stop of main waste water discharge from PCP for 10 years the surface water of the pond was self clarified while toxic compounds lay down on the pond bottom. Total mercury concentration in the surface water dropped till 0.1 mkg/l (0.5 MPC<sub>w</sub>) and fluctuates at this level depending on the waves that spread man made bottom sediments in the shallow water.

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Today the settler does not represent high risk for population and environment (except contaminated fish and biota). However potential risk still exists because of high pollutants concentration accumulated in the bottom sediment and high water level 6 m exceeding the water level in the river Irtysh.

To solve the problem of further settler operation it is required to take measures to prevent the potential risk: (i) to develop a mechanism to control the water level and (ii) make toxic compounds to deposit in the bottom sediment thus to minimize their chemical and biological activity.

### I. Control of water level

At present the elements of water balance practically unknown but judging by the high level of water in the pond at minimal waste water discharge it looks like those elements changed drastically since the pond's design and construction. It is evident that even with the stop of Power Plants operation the waste water discharge from these sites will take place for some decades. However it could happen that the flow of groundwater towards the settler will increase in the future (along with seasonal flood and rainfalls) which will bring to the emer-

gency situation under which the pond can not be used any more. It is necessary to conduct the following study of:

1. current water balance of the settler, with primary study of its underground flow and simulation of possible water balance based scenarios of its operation,
2. idea of measures to be taken to deviate the flow of groundwater from Power Plants ash lagoon,
3. possible reliable hydro isolation of new sites of ash lagoon,
4. possible use of surface water of the settling pond for technical purpose in the north industrial area, in particular in a cooling pond construction.

## **II. Control of surface water and bottom sediment contamination**

At present there is no information on number of pollutants deposited in the bottom sediment and surface water of the lake. We also don't know their biological activity and scenario of their possible mobilization in case of recommencement of pond operation both as a settler and as a cooling pond or other source of technical water supply. At the same time there is a number of technical decisions known to isolate toxic bottom sediment for surface water protection with the help of different isolation and semi-isolating screens.

The following studies should be carried out:

5. making vector map of bottom sediment contamination with different specific pollutants and computation of the sludge and pollutants stock,
6. of accessibility of bottom sediments for chemical, physical-chemical and biological mobilization as well as their classification,
7. to develop the technology of bottom isolating screen preventing the mobilization of toxic compounds laid in the bottom sediment. The screen must be penetrative for bog gases and resistant to waves. It could be materials made of local inexpensive mineral resources. It is important to develop the technology of its placement on the bottom of the lake.

01.09.06.

## 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 Demercuration 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 groundwater) 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 demercuration program shall prove the efficiency of demercuration 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 I of Demercuration 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 demercuration 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 demercuration 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 demercuration 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 groundwater. 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.