BG Chair of Environmental Technology
of Almaty Institute of Power Engineering and Telecommunication

Climate Change Coordination Centre

Ministry of Environmental Protection of the Republic of Kazakhstan

INTERNATIONAL WORKSHOP

Environmental mercury pollution: mercury emissions, remediation and health effects

May 28 - June 1, 2007

Kazakhstan, Astana
Hotel «Akku»

Supported by the International Science and Technology Centre

I S T C
М Н Т Ц

Environmental Mercury Pollution: Mercury Emissions, Remediation and Health Effects

Proceedings of International Workshop
(May 28 - June 1, 2007)

Program, Abstracts

Edited by M.A.Ilyushchenko and L.B.Yakovleva

Astana 2007

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The expected contribution to facilitate the specific area:

- restoration of former links and keeping up new contacts between scientists, authorities and enterprises from Kazakhstan, New Independent States and West countries, focused on open and comprehensiva interchange of accumulated experience and knowledge in both minimization of mercury hazard and the risk management;
- critical evaluation of demercurization projects conducted in Kazakhstan as well as exchange of plans and experience in remediation of mercury contaminated areas;
- discussion of the strategy, principles and policy of risk assesment posed by mercury effects on population health;
- discussion of the range and possible ways to decrease mecury emission to atmosphere from the countries within the region;
- establishment of basic mechanisms of knowledge transfer experienced by scientists to improve up-to-date methods of risks mitigation;
- generate proposal ideas in the above-mentioned areas of atmospheric mercury emissions, health effects and site remediation by engaging institutes of interest in Russia and Kazakhstan;
- proposals for improving scientific and equipment basis for research, control and monitoring over risks related to mercury contamination and its influence to the population health.

Objectives of the scientific workshop:

- assessment of efficiency of engineering solutions and experience exchange in remediation of areas contaminated with mercury (cases of demercurization projects in Pavlodar and Temirtau).
- application of different approaches and methodologies for assessment of mercury effects on health of population;
- assessment of mercury emissions to atmosphere (mainly due to coal and hydrocarbon fuel combustion) and the region's contribution to its global transport to the polar zone;
- development of new approaches and cost-effective technologies to minimize mercury hazard;
- design of new scientific-technological researches and discussion of new projects related to minimization of mercury hazard.

Program of International Scientific Workshop

"Environmental Mercury Pollution: Mercury Emissions, Remediation and Health Effects"

Astana, Pavlodar, Ekibastuz (Kazakhstan)
May 28 – June 1, 2007

28.05.2007

Visit to demercurization area at the territory of former PO "Khimprom" in Pavlodar city.
Meeting at Pavlodar Oblast Territorial Department of Environmental Protection.

29.05.2007

Leave from Pavlodar city for Yekibastuz city.
Attendance of open-pit coal mine "Bogatyr" and power station GRES-1 in Yekibastuz city .
Leave from Yekibastuz city to Astana city.

30.05.2007

09:30 - 10:00 am Registration of participants: "Akku" Hotel, Conference Hall

Workshop opening

10:00 – 11:00 am **Welcoming speeches:**
Kanat Baigarin, Head of BG Chair of Environmental Technology, Almaty Institute of Power Engineering, Director of Climate Change Coordination Centre, Kazakhstan,
Nurlan Iskakov, Minister of Environmental Protection of the Republic of Kazakhstan,
Nicola Kim, Program officer, Department of Foreign Affairs and International Trade, Canada,
Valentina Rudneva, Senior Project Manager, International Science and Technology Center, Russia

Session1: Remediation of mercury contaminated territories

Session Chairman – **Professor Svetlana Abdrashitova**

11:00 – 11:20 am Experience of demercurization works within the territory of PO "Khimprom", Pavlodar. Artur **Akhmetov,** JSC "Kaustik", Pavlodar, Kazakhstan, V. Bednenko, Pavlodar Oblast Territorial Department of Environment Protection, Pavlodar, Kazakhstan

11:20 – 11:40 am "Nura river mercury clean-up" project. Background, major technical decisions and course of the project realization. A. Ryabtsev, Evgeny **Lukinykh,** Committee for Water Resources of the Ministry of Agriculture of the Republic of Kazakhstan

11:40 – 12:00 am **Coffee break**

12:00 – 12:40 pm Concomitant mercury species analysis for risk assessment and mercury remediation projects. Holger **Hintelmann**, Trent University, Peterborough, Canada

12:40 – 1:20 pm "Green chemistry" approach for remediation of mercury and bioleaching of mercury using fungal-organic acids. Shamil **Cathum**, Science Applications International Corporation (SAIC), Ottawa, Canada

1:20 – 2:20 pm **Lunch**

2:20 – 2:40 pm Risk assessment from groundwater mercury pollution of the Northern area of Pavlodar industrial region by the methods of mathematical simulation. Vladimir **Panichkin,** U.Akhmedsafin Institute Hydrogeology and Hydrophysics, Almaty, Kazakhstan

2:40 – 3:00 pm Methods and technology of creation of the system of mathematical models with different scales for groundwater mercury pollution within the industrial area of Pavlodar city. Oxana **Miroshnichenko,** U.Akhmedsafin Institute Hydrogeology and Hydrophysics, Almaty, Kazakhstan

3:00 – 3:20 pm Development of technology of bioremediation of mercury contaminated groundwater for Pavlodar outskirt. Svetlana **Abdrashitova**, Institute of Microbiology and Virology, Almaty, Kazakhstan, W. Davis-Hoover, US Environmental Protection Agency, Cincinnati, R. Devereux, US Environmental Protection Agency, Gulf

Breeze

3:20 – 3:40 pm **Coffee break**

3:40 – 4:00 pm Post-demercurization monitoring and risk assessment in the Northern industrial area of Pavlodar city. Mihkail **Ilyushchenko**, Rustam Kamberov, L.Yakovleva, Almaty Institute of Power Engineering and Telecommunication, Kazakhstan

4:00 – 4:20 pm Development of integrated demercurization technology and facilities for its implementation in Kazakhstan. V.Khrapunov, B. Levintov, **Sergei Trebukhov**, Center of the Sciences of the Earth, Metallurgy and Ores Beneficiatio, RK MES, Almaty, Kazakhstan

Poster presentations

1. Selective sorbents of heavy metals based on modified fly ash microspheres. Valeriy **Drozhzhin**, L.Danilin, Federal State Unitary Enterprise Russian Federal Nuclear Center – All-Russia Research Institute of Experimental Physics (FSUE RFNC-VNIIEF), Sarov, Nizhniy Novgorod region, Russia, M. Shpirt**,** Institute of Combustible Fossils, Complex Center on Processing Solid Combustible Fuels, Moscow, Russia
2. Mercury in coals of Kazakhstan. Mihkail **Ilyushchenko**, G.Uskov, Almaty Institute of Power Engineering and Telecommunication, Kazakhstan
3. Risk to residents living near the mercury pollution at Temirtau, Kazakhstan. Hui-Wen **Hsiao**, T.W. Tanton, School of Civil Engineering and the Environment, University of Southampton, UK
4. Application of the Cost-Effective Remediation Technology for Mercury Removal from the Soil Environment in the Area of the Former Chemical Plant in Vlora, Albania. Karel **Dohnal,** J. Reif, J. Prusa, A. Liska, Pavel Blaha, Jan Pejril, GEOtestBrno, Czech Republic

31.05.2007

Session 2: Mercury emissions to atmosphere and its global transfer

Session Chairman – **Professor Mikhail Shpirt**

10:00 - 10:40 am Mercury emissions control and analysis at SaskPower. David **Smith**, Saskatchewan Power Corporation, Regina, Canada

10:40 – 12:20 am Determination of mercury isotope fingerprints for identification and tracking of mercury sources. Holger

Hintelmann, Trent University, Peterborough, Canada

11:20 - 11:40 am **Coffee break**

11:40 – 12:00 pm Mercury air emissions as a result of coal burning at Russian thermal power plants. Alexandr **Zykov**, S.Anichkov, All-Russian Thermal Institute (VTI), Moscow, S.Kolesnikov, E.Shuvalova, N. Zelinsky Institute of Organic Chemistry (IOC), Moscow, Russia

12:00 – 12:20 pm Preliminary evaluation of mercury content in fossils and its distribution during treatment of coal and oil. Mikhail **Shpirt,** Institute of Combustible Fossils, Complex Center on Processing Solid Combustible Fuels, Moscow, Russia, L.Danilin, V. Drozhzhin, Federal State Unitary Enterprise Russian Federal Nuclear Center – All-Russia Research Institute of Experimental Physics (FSUE RFNC-VNIIEF), Sarov, Nizhniy Novgorod region, Russia

12:20 – 12:40 pm Development and testing of a pre-combustion technology for clean coal. Vladimir **Khrapunov**, B. Levintov, S.Trebukhov, RK MES, Almaty, Kazakhstan

12:40 – 1:10 pm Potentials of analytical mercury control in hydrocarbon fuel and other natural objects. Lev **Danilin,** V. Drozhzhin, Federal State Unitary Enterprise Russian Federal Nuclear Center – All-Russia Research Institute of Experimental Physics (FSUE RFNC-VNIIEF), Sarov, Nizhniy Novgorod region, Russia, M. Shpirt, Institute of Combustible Fossils, Complex Center on Processing Solid Combustible Fuels, Moscow, Russia

1:10 – 2:10 pm **Lunch**

2:10 – 4:00 pm **Round-table:** Discussion of submission of new project proposals on mercury hazard to ISTC.

01.06.2007

Session 3: Risk assessment and mercury impact on health of population

Session Chairman – **Doctor of biological sciences Faina Ingel**

10:00 - 10:40 am Hot spots of chronic exposure to mercury in Canada: a combination of environmental sensitivity and human vulnerability. Marc **Lucotte,** University of Quebec, Montreal, Canada

10:40 - 11:00 am	Monitoring of mercury in the environment. Evaluation of antioxidant system protecting humans in polluted environment. H. Brainina, Natalia **Stozhko**, A.Ivanova, Zh.Shalygina, E.Gerasimova, NPP "IVA", Yekaterinburg, Sverdlovsk region, Russia.
11:00 – 11:20 am	Risk assessment of human health under exposure with low-level of mercury. Faina **Ingel**, A.N.Sysin Research Institute of Human Ecology and Environmental Health RAMS, Moscow, Russia, J. Eyles, School of Geography and Geology McMaster University, West Hamilton, Canada, P. Eckl, University of Salzburg, Institute of Genetics and General Biology, Salzburg, Austria, M. Chiba, International University of Health and Welfare, School of Pharmaceutical Sciences, Tokyo, Japan, Sh. Khussainova, Scientific Center of Pediatrics and Children Surgery, Almaty, Kazakhstan
11:20 – 11:40 am	**Coffee break**
11:40 – 12:00 pm	Specificity of Diagnostics and Examination of Mercury Exposures. B. Filatov, Tatyana **Charova,** Federal State Unitary Enterprise "Research Institute of Hygiene, Toxicology, and Occupational Pathology" at Federal Medical and Biological Agency, Volgograd, Russia
12:00 – 12:20 pm	Results of investigation of mercury vapor content in hospitals. Irken **Kamberov,** R. Kasymov, N. Gorodisskaya, Renat Kamberov, Institute of High Technologies, NAC "Kazatomprom", Almaty, Kazakhstan
12:20 – 12:40 pm	Mercury containing waste as source of environment pollution by mercury: hygienic evaluation and demercurization. Mikhail **Korshun,** Hygienic Regulation Committee of Public Health Ministry of Ukraine, Kiev
1:00 – 2:00 pm	**Lunch**
2:00 – 3:00 pm	**Workshop closing:** Sessions chairmen speeches Discussion Decisions making on the workshop results

Welcoming Speech of Mr. N.A. Iskakov, Minister of Environment Protection of the Republic of Kazakhstan

I would like to welcome at the capital of the Republic of Kazakhstan, Astana City, participants of international workshop **"**Environmental Mercury Pollution: Mercury Emissions, Remediation and Health Effects**"**. I hope it will meet expectations of its organizers and facilitate cooperation between scientists and specialists in different countries dealing with mercury contamination issues.

Place and time of this workshop were not chosen randomly. Most countries of the former Soviet Union, due to political and economical reformations, experience economic growth accompanied by industrial restructuring. Many industries that faced difficulties or were stopped at late 90's, at present go through reorganization process, change of technologies or shift production outputs. Instead of plants, rehabilitation of which was economically not feasible, there appear new competitive enterprises. It is very good when this process is accompanied by recovery of the environment through use of cleaner technologies, adherence to strict environmental norms and change in behavior of government and society relating to environmental issues. But there is still a problem of historical pollutions, solving of which demands huge financial resources, new knowledge and modern technologies on rehabilitation of the environment. Mercury contamination issue, due to high toxicity of this metal and its compounds as well as due to broad use of high volumes of mercury in technologies of the second part of the 20th century, is one of the most critical environment protection goals.

Kazakhstan inherited two large historical mercury contamination sites in Temirtau and Pavlodar. Both of them appeared due to use of "dirty" technologies, use of which, is being stopped all around the world: acetaldehyde and chlorine-alkaline technology using amalgam method. Threat of the situation is that two Kazakhstani rivers Nura and Irtysh, that are very important sources of water supply in our water-poor country, were endangered to be contaminated. Therefore, even in most difficult years of economic crisis, President Nazarbayev and the Government paid a lot of interest to find means and ways to eliminate both sources of contamination. To perform the most urgent mercury elimination activities we studied possibilities to get financial and technical support from western countries and international organizations. This support was received first of all from European Union that funded through international programs INCO-Copernicus and INTAS scientific and research activities that are being performed at present. Society of scientists from Kazakhstan and the Great Britain, as well as from some other European countries with support of BG Kazakhstan, implemented eight research projects aimed at

evaluation of scale and risks of mercury contamination at the Nura River and northern industrial zone of Pavlodar.

Project on demercuration of chlorine-alkaline production in Pavlodar, the first phase of which was completed in 2005, allowed, by using unique technology, for constructing "wall in the soil" around several pollution sources that prevented mercury penetration into the Irtysh River and underground waters in the region of water intake facilities. At present we study possibilities to perform phase II of the project related to cleaning the upper soils from elementary mercury at the site of former Khimprom, as well as minimization of wastewaters at Bylkykdak. Kazakhstani contractors perform this project from state budget of the Republic of Kazakhstan.

The project on cleaning the Nura River includes cleaning territories in western industrial zone and Temirtau suburbs as well as prevention of mercury contamination of Astana region and Kurgaldzhino natural reserve. It is financed from grants and loans of the World Bank and implemented mostly using foreign consultancy and contractors.

At both projects we are interested in evaluation of mercury impact on population living at these regions as well as on technical personnel of these productions and mercury cleaning activities. Not everything was good during their implementation. For example, in Pavlodar, due to stop of works in spring 1998 on dismantling electrolysis shop and started mercury evaporation we had to announce emergency situation and collect the spilled mercury in extreme conditions. But Kazakhstani specialists gained large experience in cleaning mercury contaminations, which as we hope will be discussed and utilized while implementing other environmental projects in Kazakhstan and worldwide.

This experience on cleaning mercury contaminations showed us that we paid not enough attention to scientific and research works on assessing existing risks to the environment and population. As a result, due to lack of modern chemical and analytical laboratories, capable to do the necessary analysis, we experience difficulties in monitoring the on-going cleaning activities. As a result, due to lack of modern chemical laboratories capable to do the necessary analysis, we face difficulties in monitoring existing cleaning works. It is also difficult to assess the volume of necessary cleaning works because we do not have enough data on hazard level of different mercury forms and its compounds to assess cleaning criteria. Of course we are also interested in how to minimize risks for population before completion of the cleaning works.

Kazakhstan is one of the biggest coal producing and exporting countries and plans to expand use of coal for energy and metallurgy sectors. We have preliminary data that Kazakhstani coals have less mercury content comparing to klarke. We would welcome researches evaluating mercury emissions into atmosphere from combustion of mineral fuels as well as from metallurgy, gas and oil processing plants. These

researches can be very useful for developing safety measures for personnel of these enterprises and decreasing the global mercury threat.

Problems of demercurization of industrial objects within the former USSR

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In the second half of XX century mercury use increased abruptly in technological processes especially in the chemical industry within the USSR as well as all over the world. As a result despite tightening mercury normative documents and safety guidelines in the 1970s and introduction of restrictions on mercury use in industry at the end of 1980s considerable amount of mercury polluted the environment. In the middle of 1990s industrial recession stopped this process however when closing down industrial enterprises in conditions of economic and political crisis scale contaminations of environment with mercury were committed while dismantling and utilization of equipment and uncontrolled wastes burial. Complete picture of what has happened starts clearing up only now when data about technogenic releases of mercury have been published as a result of investigation of the areas of contamination. The matter concerns mercury losses in the order of thousands tons at each of such large-capacity productions as chlor-alkali production within PO 'Kaustik" or "Khimprom" and several hundreds tons at chlor-alkali productions within vitamins and wood-pulp factories, chemical reagents plants, at acetaldehyde and amalgam productions as well as productions of luminescent lamps, thermometers etc. In fact at present any of industrial centers are sources of mercury contamination first of all of surface water and groundwater and also atmosphere because of evaporation of metallic mercury from contaminated soils and wastes storages.

As long as mercury had commercial value closing of productions using mercury was followed by metallic mercury collecting and utilization of wastes rich in mercury (PO "Khimprom", Sumgait city – in the early 1980s, PO "Kaustik", Sterlitamak city – in the late 1980s). In the 1990s wastes reach in mercury such as heavily contaminated equipment, building structures, sludge and soils were buried already without removal of mercury (PO 'Khimprom", Pavlodar city). Treatment of soils and bottom sediments less contaminated with mercury has remained yet a matter of discussions at the stage of feasibility study working out. Within the former USSR there has not been any example of carrying such a task to its practical implementation because it seems unfeasible to reach MPC_s for mercury (2.1 mg/kg) in present-day economic conditions.

At present Kazakhstan is the only country which conducts remediation works (at industrial areas of the former PO "Khimprom", Pavlodar city and PO "Karbid", Temirtau city) despite growing public realization of importance to cease productions which still use mercury and

necessity of demercurization of the closed enterprisers as well as areas around them. The main obstacle to demercurization works is absence of correct data on assessment of mercury impact on environment and public health at the polluted areas. Usually only international organizations finance researches conducted in this direction but on limited scale. It is worth mentioning extremely restricted number of new chemical analytical laboratories which have up-to-date equipment and highly qualified personnel are capable to carry out such kind of research and some degradation of laboratories which have managed to survive since the soviet time.

Abstracts of Session1:

Remediation of mercury contaminated territories

Experience of demercurization works within the territory of former PO "Khimprom", Pavlodar

A.D. Akhmetov[1], V.A.Bednenko[2]
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The first phase of demercurization of chlor-alkali production at a former PO "Khimprom", Pavlodar (operating period – 1975-1993, assessed amount of mercury losses – more than1000 tons) was completed at the beginning of 2005. It included dismantling and utility of processing equipment and mercury contaminated production buildings, manual collection of metallic mercury, removal of one-meter thick topsoil layer heavily contaminated with mercury, isolation of main underground sources of elemental mercury from atmosphere and groundwater, construction of a landfill for storing low contaminated wastes and construction materials, construction of a plant for mercury removal from concrete. In spring of 1999 when the roof of an electrolysis shop had been dismantled intensive evaporation of spilt metallic mercury started. The territory of the factory was announced as a zone of emergency which persisted for two months until completion of dismantling of the electrolysis hall and collection of the most amount of mercury (17 tons). At present post-demercurization monitoring of groundwater, ambient air and soils designed for 15 years is been conducted at the industrial area of the Chemical Plant which is expected to give a conclusion about sufficiency of the measures undertaken. Also there is being conducted an investigation of the wastewater storage pond Balkyldak (with capacity of 60 millions of m^3) located 5 km far from the Irtysh River and which can become the object of the second phase of demercurization.

The initial demercurization project involved removal of the most amount of mercury accumulated under the electrolysis shop (about 900 tons) using both hydro-separation of mercury contaminated soils and thermal removal of mercury from concrete foundation cobbings of the shop. However low cost of mercury at the world market made it expedient to change the strategy of mercury removal to more cost-effective strategy of containment of the main sources of mercury contamination.

Soils heavily contaminated with mercury (hotspots) were isolated on their perimeter from groundwater with help of anti-filtration screen so called cut-off wall which was deepened into layer of basalt clay at the depth of down to 20 m. The cut-off wall was 0.6 m thick and made bentonite-like clays with a filtration coefficient not more that 10^{-7} cm/s. The cut-off wall was constructed using a unique excavator equipped by

clamshell scoop on a vertical pole. Total length of cut-off wall has amounted to 3588 m.

Sources of contamination in site of buildings of chlorine production were isolated from atmosphere by placing and compacting bentonite-like clays above contaminated soil layer and in site of the storage for liquid mercury wastes and sludge – by constructing a multi-layer cap. The landfill for mercury containing solid wastes was located 50 m far from the electrolysis shop. It was a pit down to 3 m deep lined by clay not less than 0.5 m thick with a filtration coefficient of 10^{-7} cm/s where construction materials containing mercury not more than 1% were put and filled up with soil-concrete solution. Formed monolith was covered with asphalt cap to prevent dusting. The area of the asphalt cap has amounted to 15810 m^2.

"Nura River Mercury Clean-up" Project. Background, Major Technical Decisions and Course of the Project Realization

A.D. Ryabtsev, **E.G. Lukinykh**
The Committee for Water Resources of the Ministry of Agriculture of the Republic of Kazakhstan, Astana, consultants_astana@nursat.kz

1. Background of Nura River pollution problem. Organization of production at JSC "Karbid". Ways of wastewater disposal. Scale of the pollution.

2. Studies conducted and their sequence. Procedural issues of attracting grants and loans. Making decision on necessity of clean-up works.

3. Project Components, basic technical decisions. The project organization concept.

4. Problematic issues. Insufficient exchange of experience and information on international projects including that on mercury effect on human health. Insufficient equipping of laboratories as well as scope of environmental monitoring works. Difference in methodology and standards.

5. Current status of the project. Organizational management. Implementation plan on years. Extra realized actions, necessity of which was approved in the course of their practical implementation.

Risk assessment from groundwater mercury pollution of the Northern area of Pavlodar industrial region by the methods of mathematical modeling

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This report analyses the results of the investigations executed within the framework of the project INCO-Copernicus ICA2-CT-2000-10029 " Development of cost-effective methods for minimizing risk from heavy metal pollution in industrial cities: A case study of mercury pollution in Pavlodar " as of mathematical modeling of groundwater mercury pollution in the Northern part of Pavlodar industrial region.

The hydrogeological conditions of the modeling region, existed on the conditionally undisturbed period for the year of 1970 is outlined. Considerable change of conditions under the influence of technogenic activity – construction of Balkyldak and Sarymsak waste waters storage ponds, ash lagoon for combined power stations (CPS) No 2 and 3, a chemical plant, oil-processing and some other industrial objects, putting into operation of magistral irrigation channel, of irrigation missives etc. are described.

It is noted that beginning from the year of 1975, after putting into operation of the Pavlodar chemical plant, intensive pollution of groundwater has begun in the result of numerous mercury losses at the building 31, and also the leakages of mercury containing industrial wastes from communications. Groundwater flow forming at the region of the ash lagoon of CPS No 2 and 3, goes under the building 31, is polluted with mercury and transports it into north-western direction. This creates the real danger of mercury appearance in the waters of the Irtysh River, situated within the distance of 5 km to the north-west of the chemical plant, and also into water supply wells and draw-wells of the village Pavlodarskoe, the inhabitants of which use groundwater for water supply. The aim of the modeling was the groundwater mercury pollution plume distribution forecasting for mercury appearance danger estimation into the Irtysh River and into wells of the village Pavlodarskoe, and for measures development of risk lowering.

Results of hydrogeological conditions schematization on the model, methods of its development and calibration, formulation of forecasting of tasks and results produced are described in this report. There were executed 4 variants of forecasting for the period of 30 years on this model. The first variant presupposed the conservation of the existing pollution sources, second one – source localization under the building 31

with mercury electrolyzes, as it is foreseen by the original program of chemical plant territory demercurization. In accordance with the third variant the existing hydrogeological conditions were changing. Water supply break off from the Irtysh River onto northern industrial region was imitated. There will be no losses of technical waters from magistral water ducts in this case. This, in its turn, will lead to groundwater flow direction change, and therefore to their pollution plum transportation direction change. The fourth variant of the prognosis was fulfilled under the condition of the total localization of the two basic sources, situated correspondingly under the building 31 and at the pump station region earlier executing the transfer of mercury-containing industrial wastes into wastewater storage pond Balkyldak.

Based on the results of the investigations executed, conclusion has been made that without considerable additional intervention, capable to unfavorably change the hydrogeological conditions existing now in Northern industrial area of Pavlodar, and also the conclusion that the plum of groundwater mercury pollution is not dangerous during the nearest decades to the Irtysh River and to the inhabitants of the village Pavlodarskoe. Isolation of the basic sources of mercury under the building 31 and in the area of the former wastewater pumping station with the help of anti-filtration screen of the type "cut off wall" will stop the further processes of mercury sorption by water-baring rocks and it does not exactly enough imitate groundwater pollution plum distribution in section. This model must be more detailed for gaining more exact results.

Methods and technology of creation of the system of mathematical models with different scales for groundwater mercury pollution within the industrial area of Pavlodar city

O.L. Miroshnichenko

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Regional model of the hydrogeological conditions of the Northern industrial area of Pavlodar city has been produced within the framework of the Project INCO-Copernicus ICA2-CT-2000-10029 "Development of cost-effective methods for minimizing risk from heavy metal pollution in industrial cities: A case study of mercury pollution in Pavlodar for forecasting of groundwater mercury pollution plum distribution, and also for development of the measures as of risk lowering.

Regional model has not taken into consideration the processes of mercury sorption by water-containing rocks which does absolutely increase migrational model solution error. It has not also succeeded with enough degree of accuracy to imitate mercury pollution plum distribution

in section because of simplified schematization of hydrogeological conditions. Besides it has not been found out the connection of the modeling region with lower-situated aquifers. Specification of the regional model has been found impossible as of technical reasons. Therefore it has been adopted the decision about production of a local model which in horizontal projection includes only the territory of mercury pollution plum distribution. It has been in detail reproduced the lithological composition of hydrogeological object and have been taken into consideration the mercury sorption processes by water-bearing rocks.

Sorption processes in clayish rocks are taking place basically in thin near-boundary layer of sorbing rocks. Clayish rocks for imitation of this effect on the model in section have been schematized in the form of some layers. Total quantity of layers for local model was 19. Modeled region in horizontal projection was approximated by grid with size of 113x92.

Determination of the boundary conditions is the basic problem during development of the local model. There are given coming from the solution of hydrodynamic task, received on the regional model. Some criteria are separated for the estimation of the rightness of the assigning of boundary conditions and parameters of the local model. Balance components of the flow of groundwater, calculated on local and regional models, must coincide. Value of water conductivity of each layer of the regional model must be equal to the value of total water conductivity of its componental layers in local model. Values of parameters of local and regional models must be adequate. Establishment of boundary conditions is a very labor-intensive procedure, for the automation of which the special complex of software was developed. There are discussed in this report the methods and automated technology of modeling developed by this author, on the system “regional model – local model”, application of which has allowed to considerably lower time expenditures.

The system of models created more accurately reproduces hydrogeological conditions which will allow receiving more accurate solutions of tasks of prognosis. Now its calibration is on the final stage.

Investigation is carried out within the framework of the ongoing project of ISTC 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”.

Post-demercurization monitoring and risk assessment in the Northern industrial area of Pavlodar city

M.A. Ilyushchenko, R.I. Kamberov, L.V. Yakovleva
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Post-demercurization monitoring at the place of mercury contamination in Pavlodar city is being carried out on ISTC K-1240p project launched in 2005. When conducting demercurization works in 2002-2004 necessity of such kind of research was caused by application of containment of sources of mercury contamination strategy instead of removal one followed by treatment of mercury contaminated materials. Three main sources of mercury contamination in Pavlodar where more than 1000 tons mercury is deposited: soils around (i) the building 31 and (ii) the wastewater pumping station including their concrete foundations as well as (iii) the storage place for mercury containing wastes were isolated from groundwater with help of a clay antifiltering screen so called "cut-off wall" reaching basalt clays at the depth of down to 20 m. Containment from atmosphere was done using in one case (iii) – multi-layer turf-covered cap, in the second case (i) – clay cap 0.5 m thick and in the third case (ii) – the cap was not constructed at all. Mercury contaminated building structures of dismantled buildings and facilities were placed into specially developed pit dug at the industrial area which was filled up with cement solution and consolidated as concrete monolith. From the top the landfill was covered by clay layer and asphalted.

The results of determination of mercury concentration in soil samples taken within the industrial area of former chlor-alkali production and in site of the wastewater pumping station 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_s being 2.1 mg/kg) keep up here after implementation of demercurization works both on the surface of clay caps 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 ranged from 100 to 1600 ng/m^3 (the average daily maximum permissible concentration in atmosphere MPC_{ad} equal to 300 ng/m^3 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^3) 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.

The results of determination of mercury concentration in groundwater at the area of mercury pollution were inserted onto the vector map together with the results of similar research of 2004 and 2005. This map showed dynamic of total mercury concentration change in groundwater in post-demercurization period and 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 the 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 ranged from several ng/l to tens of ng/l that averaged 0.01% of total mercury concentration.

Development of technology of bioremediation of mercury contaminated groundwater for Pavlodar outskirt

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Northern outskirt of Pavlodar city is heavily polluted with mercury as a result of activity of former PO “Khimprom”, which used to produce chlorine and alkali in 1970s-1990s using electrolysis based on amalgam method. Its activity has resulted in pollution the region with mercury and formation of a plum of groundwater mercury contamination. There is possibility that the plum of mercury contamination can reach the Irtysh River which is 5 km far from the plant and serves as a water supply source for some cities of Kazakhstan and Russia. This poses significant risk to health of population in this region.

Research on ISTC K-756p project enabled to isolate resistant to mercury aerobic, facultative-anaerobic and anaerobic sulfate-reducing bacteria from contaminated soils and sediments of Pavlodar outskirt, to characterize them and also to show that mercury can be removed out of

groundwater with help of these aerobic and anaerobic bacteria being colonized on some support materials. Some of properties of these isolates enable to be used for development of *in situ* technologies to mitigate environmental consequences of groundwater mercury contamination.

ISTC K-1477p project which is about to be launched is a continuation of ISTC K-756p project and schedules to conduct both enlarged laboratory trials using bioreactors of pilot dimensions in order to optimize conditions for mercury removal with restricted generation of soluble methyl mercury and small-scale field trials at the place of the pollution. Native bacteria cultures adapted to environmental conditions at the place of contamination will be used. This approach can lead to development of cost-effective technology of groundwater cleanup from mercury.

Development of integrated demercurization technology and facilities for its implementation in Kazakhstan

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Toxic mercury is one of the most challenging environmental problems we face today. Areas of heavy mercury pollution are located in Pavlodar and Temirtau (Kazakhstan).

The Republic State Enterprise "Center of the Sciences of the Earth, Metallurgy and Ores Beneficiation" (RSE "CSEMOB") in Almaty, Kazakhstan has developed a unique vibro-vacuum assisted technology and continuous operating equipment aimed at processing of mercury-containing minerals and anthropogenic raw materials. Through numerous "know-how" components engineering and environmental performances of proposed technology and facilities are considerably superior to vacuum batch systems operating under atmospheric pressure.

Technology and equipment performances have been tested in soils demercurization at Pavlodar Chemical Plant facilities using a combination of vibration, vacuum and thermal energy effects.

This work was the subject of a successful ISTC K-526p project. In-process tests of the plant of 350-kg/day capacity resulted in direct mercury removal over 94.61 % (residues contained 0.002-0.004 % Hg) at 440-450^{0}C temperatures and 4-kPa pressures. In-process test of worked-out fluorescent lamp phosphor demercurization at proposed pilot vibro-vacuum assisted plant of 500-kg/day capacity proved higher degree of mercury removal (over 99%).

Industrial coals pre-combustion to remove mercury are associated with coals desulfuration and moisture removal resulting in improvement of coals caloric value. Feasibility of proposed demercurization technology

and facilities has been proved by laboratory studies on trial samples (USA, Dakota coal samples).
High efficiency (over 98-99%) of acetaldehyde production sludge demercurization has been proved by sludge (JSC "Karbid", Temirtau) processing results, which evidenced higher degree of mercury removal.

Application of the Cost-Effective Remediation Technology for Mercury Removal from the Soil Environment in the Area of the Former Chemical Plant in Vlora, Albania

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Locality characteristic (Vlora, Albania):
Former chemical Cl- PVC plant is situated close to the seashore, 4 km from the centre of Vlora city. The plant began operation in Vlora (Albania) in 1972. One of the process units - the electrolytical process for chlorine production used mercury cathodes. Mercury cathodes were used for the processing of caustic soda, chlorine and hydrogen. Almost three kilograms of mercury leak off from each ton of processed caustic soda. There was made 190 thousands of tons of caustic soda, what means about 500 tons of released mercury. Released mercury migrated to the building constructions, soil environment, groundwater, sea and sea-shore sediments in the Vlora bay – Adriatic Sea (by the waste water), thanks to the uncontrolled waste disposal. The plant finished operation in 1991 and technology was gradually removed.

GEOtestBRNO, project description:
Comprehensive former plant area investigation, focused to the mercury contamination – **proposition of the remediation technology (principle of soil environment wash, utilize the different specific gravidity of Hg and soil particles)** – construction of the remediation technology – technology pilot test – technology long-term operation – additional sampling and analysis.

Remediation technology basic description:
A technology of phase demercurization developed in the company GEOtest Brno, a.s. can be uniformly used to extract mercury from soils. This technology was created by interconnecting three industrially proven technologies. The preliminary technology is the disintegration of clayey and sandy sediments and sludge, rocks, or disintegrated building materials with an open grain in aqueous medium. It is followed up by the technology for disintegration of material to the level of grain opening. The subsequent

technology is the gravitational separation of metallic liquid mercury on the basis of the difference in unit weight.

Presentation context:

Description of the investigation provided by the company experts

- literature search, proposal of the project works
- geological, geochemical and geophysical investigation, building documentation
- maps of contamination and other outputs – use of Atomic Spectrometer RA 915+

Technology description

- presentation of the technology principle
- description of the basic technology parts – photos and short film

Experience with the long term operation:

- description of the remediation technology operation
- description of the all necessary inputs (expert ensure, electric requirements, water management)
- adaptation for the local conditions
- results of the long term operation (technology efficiency, designed capacity, advantages in comparison with standard remediation technologies)

Abstracts of Session 2:

Mercury emissions to atmosphere and its global transport

Mercury Emissions Control and Analysis at SaskPower

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Saskatchewan Power Corporation (SaskPower) is a vertically integrated electric utility owned by the Canadian province of Saskatchewan. SaskPower has a total generating capacity of 3700 MW comprised of a mixture of hydroelectric, natural gas, wind and lignite coal generation. There are abundant lignite reserves in Saskatchewan and SaskPower expects to rely on lignite to generate electricity well into the future. In order to meet future environmental requirements SaskPower is conducting a feasibility study on building a clean coal generating unit that would emit virtually no air pollutants. In addition, over 95% of the CO2 produced by that unit would be captured. Current plans are for the CO2 to be placed in near-by oil fields to enhance oil production there.

SaskPower's existing lignite-fired units face an array of emissions reductions requirements including a 40% reduction in mercury emissions by 2010. Because mercury is especially difficult to remove from lignite flue gases for a variety of reasons, SaskPower has constructed an Emissions Control Research Facility (ECRF) at its Poplar River Power Station to conduct of several mercury-control technology demonstration projects.

SaskPower has installed three Canadian-developed continuous mercury emissions monitoring systems (CMMs) at the ECRF. These systems are located upstream and downstream of where the mercury control reagent is introduced so that an ongoing determination of mercury capture efficiency can be achieved and are capable of determining elemental and total mercury concentrations in the flue gas. (The difference between these values would be oxidized mercury.) The CMMs are very complex with numerous components to extract, condition, transport and analyze flue gas mercury. These systems can provide accurate mercury determinations and are well suited for research purposes. However, intense maintenance is required to do this and deploying these systems for routine emissions monitoring would be very difficult. SaskPower has also gained considerable expertise in analyzing mercury in coal and power plant solid by-product streams. This kind of analysis can be very reliable and should be well suited for routine determinations of power plant mercury emissions.

The mercury-control research has focused primarily on activated carbon injection into a fabric filter installed downstream of an electrostatic precipitator (ESP). Up to 90% mercury removal has been seen during tests

at the ECRF. However, increased pressure drop across the fabric filter bags is a cause of concern. SaskPower has recently conducted a series of tests where treated activated carbons are injected directly into an ESP. Based on these tests a full-scale activated carbon injection system has been installed at one of the units at Poplar River Power Station and a long-term test program was started in April of 2007.

Mercury air emissions as a result of coal burning at Russian Thermal Power Plants

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Coal burning is one of more important source of anthropogenic mercury air emissions in the world. Now coal share in Russian heat-and-power engineering is about 20%. In the near future the considerable increase in coal consumption is expected. In spite of this the investigations of mercury air emissions from coal-fired Thermal Power Plants (TPPs) haven't been properly paid attention to. VTI together with Institute of Ecological Researches IVL (Sweden) have estimated mercury air emissions from the biggest TPPs of Russia after decision making in the framework of Arctic Country Council where Russia is a member about realization of actions connected with reduction of contaminants emission including mercury. In concordance with researches weighted average value of mercury content in Russian coals is estimated to be about 0.08 mg/kg. At that the content is determined substantially by average mercury concentration in the coals of Kuznetsk Basin where half of total mercury quantity from Russian mined coals is contained. Total mercury content in the coals burned in 2002 was found to be more than 6 t/y taking into account coal types and mercury proportion in coals. For initial estimation we used the conversion factor of 0.81 reflected mercury transfer from coals to flue gas. Under such assumption mercury emissions to atmosphere from 129 Russian biggest TPPs was about 5 t in 2002.

Gas cleaning equipment of Russian TPPs isn't effective for mercury catching because of high mercury volatility. Experimental data is absent in this area. VTI together with ISTC conduct researches connected with studies of mercury catching efficiency for various types of fly-ash collectors. In the near future researches of wet scrubbers with closed-cycle spray liquid system will be conducted at Tolliatti TPP. We suppose to investigate the opportunity of mercury catching increase in scrubbers with the help of injection of various agents in spray water. In future we are planning to conduct similar investigations for electrostatic precipitators and bag filters with use of special adsorbents for mercury catching.

Preliminary evaluation of Mercury content in fossils and its distribution during treatment of coal and oil

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1. Average content of mercury in coals (0.15 g/t) and shale oil all over the world is much higher than its clarke in the earth's crust and clay minerals. Estimations of average mercury concentrations in the oils of the Earth are even higher (about 2 g/t), though these values, in our opinion, are overstated and need specification. Mercury content in fossils varies a lot and is very irregular. For example, in different coal-fields it can range from 0.003 to 0.1 g/t, and in some areas of the coal-fields the content can reach more than 1.5-2 g/t, at that mercury contents can be 100-200 times different within the same coal field.

2. Industrial enrichment of coals makes it usually possible to reduce the mercury content by not more than 30% in the concentrates forwarded to burning. In processes of oil refining the main amount of mercury is concentrated in high-boiling fractions (black-oils) that are usually forwarded to thermoelectric power station to be burnt.

3. When fossils burning mercury distribution between solids captured by flue gas sanitary treating plants and gaseous products emitted to the environment depends on many factors (parameters of combustion and design of furnace plants, coal composition etc). As a rule, its main quantity goes to atmosphere together with gaseous products.

4. There could be suggested some measures to facilitate drastically reduction of Hg emissions to the environment when burning fossils.

Development and Testing of a Pre-Combustion Technology for Clean Coal

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Mercury is released to an environment as a result of many industrial processes but the largest contributor to anthropogenic mercury in the environment is from coal-fired power plants. Naturally occurring concentrations of mercury in coal vary widely but can be as high as 0.7-2.5 mg/kg. When the coal is burned to have electric or thermal energy the

mercury evaporates and enters the atmosphere in a gaseous form. From there it can be deposited through precipitation, and converted to highly toxic organo-mercury complexes that become concentrated through bioaccumulation, eventually impacting humans through consumption of contaminated foods.

Coal also contains significant concentrations of sulfur, which when combusted can form sulfur dioxide, a major contributor to environmental pollution in the form of acid rain. In addition, coal naturally contains moisture, which reduces its heating value.

This process removes mercury, sulfur and moisture from coal before it is burned, thereby significantly reducing emissions of toxic mercury and other pollutants and improving at that its value as a source of energy.

The prior studies on trial samples (USA, Dakota coal samples) proved that the Vibro-Vacuum Thermal Desorption (VVTD) processing of granular and pulverized coals with initial mercury content up to 1.19-1.5 mg/kg at temperatures up to 400-800 ^{0}C and pressure of 0.13 kPa resulted in mercury content decreasing down to 0.02-0.07 mg/kg, the volatile matter yield having been up to 37.6-39.8% and 41.6-49.5% for pulverized coals and granular coals, respectively. Given that the sulfur content in initial coal samples varied from 0.63 % to 0.72%, and its behavior in process running was ambiguous, further thorough studies are required.

Accumulated experience in the design efforts in the area of the loose materials demercurization and laboratory studies on the industrial coals demercurization evidence that the continuous vacuum-assisted system based on the use of Vibro-Vacuum Thermal Desorption (VVTD) process makes it possible to remove mercury, sulphur and moisture from the coals at industrial scale.

Potentials of analytical mercury control in hydrocarbon fuel and other natural objects

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1. Chelating resins – a relatively new type of ion-exchange materials - are more and more widely used at present to separate and concentrate various elements from the environmental objects. It is mostly their selectivity that makes it possible to perform efficiently analytical

operations, separate and selectively concentrate elements close in their chemical properties.

2. In the broad sense chelating resins are polymer organic matrices that in macromolecular chain have various functional groups of high affinity to ions of metals including very toxic ones, such as lead, cadmium, mercury etc.

3. Selective sorbents with the improved kinetic properties in the form of films (less than 1 micron thick) were created in RFNC-VNIIEF; they contain groups of 3.5dimethylpyrazole, rhodanine, thiourea, iminodiacetic acids etc. Thin-film sorbents on the basis of perchlorovinyl matrix that contain thiourea, formaldehyde and 8-oxyquinoline are most effective to determine the mercury content. Ratio of the film enrichment with mercury is $\sim 10^{2}$.

4. Method of Total X-Ray Fluorescence (TXRF) is the most promising for quantity analysis of the analyzed elements in film sorbents. It makes it possible to determine 10^{-5}-10^{-8} g/g of a substance. Implementation of method (TXRF) based on the effect of full external reflection of X-ray beam that excites the fluorescence of the sample allows reducing the detection limit of the substance down to $\leq 10^{-9}$ g.

Mercury in coals of Kazakhstan

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Small initiative research on Central Kazakhstan coal samples collecting and their analysis for mercury content was conducted in 2002-2003. The values below are lower considerably than average mercury content in black coals (0.2±0.04 μg/kg) /1/. As we are aware it is the first of such studies of Kazakhstan coals. It can become grounds for more extensive study of mercury emission during coals (and other kinds of fossil fuel) combustion within Asiatic territory of the former USSR.

Digestion of coal samples ground to particles of 1 mm in size was made by heating in boiling water-bath after addition of acid mixture of 3 $HCl + HNO_3$ (aqua regia) for 2 hours. Solution was made up to the marked level. Then aliquot of the solution was taken and diluted by 10 times with distilled deionized water (DDW). Analysis was performed by cold vapor method (with stannous chloride as a reducing agent) using AFS Merlin-Millennium (UK). Analysis of the coal reference material USGS CLB-1 with mercury standard content of 0.2 mg/kg conducted according to this method gave value of 0.16 mg/kg.

Coal sampling location	Hg content, μg/kg		
	first sub-sample	second sub-sample	average
1.Sheburkolsky open-pit mine, Karaganda region	6		6
2. Kuuchekinskiy open-pit mine, Karaganda region	12		12
3. Molodeshny open-pit mine, Karaganda region	11	18	14.5
4. Shahtinskaya mine, Shahtinsk town, Karaganda region	13		13
5. Dolinskaya mine, settlement Dolinka, Karaganda region	< 5		< 5
6. Kirovskaya mine, Karaganda City	5		5
7. Mine №22 “50 years of October”, Karaganda City	8		8
8. Mine №12, Shahan town, Karaganda region	186	237	212
9. Tentekskaya mine, Shahan town, Karaganda region	8		8
10. Stepnaya mine, Shahan town, Karaganda region	12		12
11. Kostuchenko mine, Karaganda City	5		5
12. Gorbachevskaya mine, Karaganda City	< 5		< 5
13. Karagandinskaya mine, Karaganda City	< 5		< 5
14. Ermentau open-pit mine, Akmolinsk region	6	6	6
15. Bogatur open-pit mine, Ekibastuz City, Pavlodar region	17	16	16.5
16. Vostochny open-pit mine, Ekibastuz City, Pavlodar region	14		14
17. Severny open-pit mine, Ekibastuz City, Pavlodar region	68		68
18. Maikubensky open-pit mine, Pavlodar region	6	6	6

Reference

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Selective sorbents of heavy metals based on modified fly ashes microspheres

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1. A wide range of sorbents based on fly ash microspheres for environmentally dangerous elements, such as fission products (FP) and heavy toxic metals (Cu, Pb, Hg and Sr) was worked out in the Russian Federal Nuclear Center. Sorbents are stable in the acid and weak alkaline media, and have good kinetic and capacity properties.
2. Surface modification of the fly ash microspheres is done with inorganic compounds (Ferro cyanides, phosphates, monoxides of 4-valent elements), and with organic reactants (rhodonite, 8-oxychinoline, thiourea, iminodiacetic acid).
3. Research on synthesis of sorbents for mercury sorption using amino-containing and silicon-containing compounds as well as sulfur derivatives as modifiers was started. The sorbents have high selectivity for mercury and can extract 100-120 mg of mercury per 1 g of fly ash microspheres.

Abstracts of Session 3:

Risk assessment and mercury impact on health of population

Hot spots of chronic exposure to mercury in Canada: a combination of environmental sensitivity and human vulnerability

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The COMERN project was launched in 2001 with the mandate to address the urgent need for the development of a framework enabling researchers, political stakeholders, and communities concerned by the mercury question to evolve towards an interdisciplinary association capable of synergistically combining our knowledge on Hg into an original synthesis and increase our potential for accurate risk communication on specific regional Hg situations. We are presently working at identifying specific hot spots of Canadian ecosystems to Hg bioaccumulation and subsequent transfer to humans. This work is based on two concepts: (1) the sensitivity of the ecosystem to bioaccumulation, induced and influenced by factors such as Hg loadings, the different transport and methylation processes, and human activities and (2) the vulnerability of the populations exposed to the contaminant, an evaluation of their early health alterations and their capacity to recover and/or to cope with the contamination, taking into account their social status and their political resources. We started to apply this approach to four distinct case studies representative of the large spectrums of both Hg contamination and Hg exposure through fish consumption in Canada, i.e. sports fishers of lakes of the boreal forest, commercial fishers of the industrialized region of Lake St Pierre (LSP), Innu nation communities in Labrador and seafood consumers of the Bay of Fundy.

Introduction

The presence of Hg in ecosystems is ubiquitous, even in the absence of local/regional contamination point sources. Almost all fish consumers (being occasional or frequent) are exposed to this contaminant. However, given the complexity of environmental processes leading to the accumulation of Hg in fish tissue, and the relative importance of fish as a protein source among communities motivated by either tradition or economic dependency, most available literature falls short to fully evaluate the regional level of risk to health (and/or the health benefits related to fish consumption) encountered by fish consumers in their day-to-day life.

Results and Discussion

Community groups, including more than 400 participants, were assembled in four distinct regions to share their knowledge and actively participate in the elaboration and progress of the research plan, such as the

identification of sampling sites actually used by fishers, the environmental characterization of Hg levels in the different environmental compartments, the description of fishing habits and pressure, the gathering of dietary, social, economic and cultural information, the evaluation of exposure through human indicators (hair and blood), the choice and application of neuro-functional tests to monitor early health alterations, and the transmission of the acquired knowledge. Our results demonstrate that averaged Hg levels in hair collected among Abitibi anglers is up to twice as high as that those of the Innu community, and even more elevated than the LSP cohort (Canuel *et al.* 2005). This surprising result obtained by COMERN's health specialists partially finds its explanation in the type of species traditionally consumed by local population, and by a specific genetic tolerance of the Innu community against MeHg assimilation (Canuel *et al.* 2005; Lucotte *et al.* 2005) For example, the Innu tend to prefer salmon, trout and Arctic char instead of more contaminated predators such as northern pike and walleye, esteemed in the other two regions. But this fact could not justify for the relatively lower exposure levels found in the LSP participants, which in turn paused an enigma to solve.

An extensive environmental characterization plan was concurrently accomplished in the four regions. Surprisingly, top predator fish species exhibit lower Hg levels in LSP than in the pristine Abitibi lakes. In fact, by examining all fish data gathered in relation with regional fish growth rates, it clearly appears that Hg dilution in fish tissue occurring in faster growing specimens generates lower Hg levels for a specimen of the same size (Simonneau *et al.* 2005). This finding could have major implications in future fishing management strategies, knowing that the fishing pressure imposed to lakes decreases competition for food within the ecosystems, which in turn favors faster growth rates.

Thus, a proper dosage of the fishing intensity applied to lakes could tend to improve the quality of fish with respect to Hg and probably other contaminants.

Conclusion

The combination of state of the art research having course through transversal case studies, led by this expert-group, provides a unifying level of science by gathering researchers around a global vision of the Hg issue on a regional level while helping identify new gaps of knowledge by forcing the integration of all hierarchical levels of the ecosystems science toward the characterization of its vulnerability to Hg contamination. This frame of work stresses the role of humans as an important part of the ecosystems, which must not be set-aside during the course of environmental studies. In fact, the main conclusion being drawn to date from the comparative research described above is that human behavior could be the most important factor setting respective exposure

levels to Hg of participating communities. Furthermore, sustainable management of resource such as adequate fisheries practice can be put in place to lessen impacts exerted by Hg on ecosystems. We are convinced that the trans-disciplinary approach presented here establishes a new pattern for future efficient and conclusive studies and regional risk communication strategies on the Hg issue, which might be viewed as the most important accomplishment achieved through this research.

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Monitoring of Mercury in the Environment. Evaluation of the Antioxidant System Protecting Humans in the Polluted Environment

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Mercury is among the most toxic environmental pollutants. Mercury (II) ions can form stable complexes with biologically important molecules. The interaction of mercury with thiolic groups of glutathione and cysteine causes a sharp degradation of the human protecting antioxidant system and, as a result, intensive formation of free radicals in cells. The excess concentration of free radicals leads to pathological changes in the human organism. Therefore it is very important and topical to monitor the concentration of mercury in various environmental objects. It is also necessary to study the toxic effect of mercury on the antioxidant activity of biological fluids in the human organism.

In many countries mercury measurements are included in programs aimed at monitoring the man-made pollution of various natural objects. The inversion voltametric (IV) method is used for analytical monitoring of mercury concentrations in natural objects. However, the available electrodes do not

provide a high accuracy, sensitivity and selectivity of mercury measurements. A highly sensitive electrochemical sensor responsive to mercury (II) ions is developed. It is easy to use and does not require any preliminary treatment before measurements. A high electrochemical reactivity of the developed sensor is explained by ultramicro- and nanoparticles of gold present in its modifying layer. Methods for determination of mercury in soil and in natural, drinking or sewage water have been elaborated and certified.

The existing methods for evaluation of the general antioxidant activity of various biological media are laborious and slow. Moreover they require highly qualified operators, the use of expensive equipment, and have been realized only in research laboratories. A new potentiometric method for evaluation of the antioxidant activity (AOA) of biological fluids by means of a mediator system is developed. The proposed method is distinguished for rapidness, simplicity and availability of equipment. It does not require expensive reagents and highly qualified operators and can be used for population screening.

The scientific, production and introduction enterprise "IVA" LLC has developed and commercially produces "IVA-5" voltametric analyzers and "MPA-1" potentiometric analyzers for determination of mercury in the environment and evaluation of the antioxidant activity.

The specialists of Russian Federal Nuclear Centre – All-Russia Research Institute of Technical Physics (Snezhinsk) take part in the development of these analyzers.

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Risk assessment of human health under exposure with low-level of mercury

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Practically everybody on Earth is exposed to low doses of mercury. However, the associated risk can be expected to vary between individuals depending on real influence and on differences in genotype,

since organic compounds of mercury - having the most toxic and genotoxic activity - are eliminated from the human body as glutathione (GSH) conjugates. GSH production is mediated by glutamyl-cysteine ligase (GCL) and conjugation by glutathione S-transferases (GST) which activity varies considerably in human populations. Besides mercury can increase the sensitivity of the genome to the action of other potentially harmful compounds. Therefore it is proposed to design and carry out an adequate research approach aimed to evaluate the complex effects of low-level mercury exposure on human health. The research consortium consisting to date of 3 countries - Kazakhstan, Ukraine and Russia - will carry out an epidemiological study among workers having professional contact with mercury (in total approximately 3000 persons) to obtain a general database (the criteria will be discussed). As a result cohorts of families of workers with children born after exposure of the fathers for not less than 5 years (about 50 - 100 families in each country). In addition cohorts will be selected for comparison as case-controls. These cohorts will be investigated as follows: 1) medical-toxicological and psychological examination as well as definition of socio-economic conditions of family, 2) analysis of genetic polymorphisms of GST (M,P,T) genes, 3) chemical analysis of mercury content and the content of other toxicants and genotoxicants in biosubstrata as well as food, water, air and soil, 4) definition of indicators of genome instability and individual susceptibility as measured by micronuclei test with cytochalasin B, 5) correlation and factorial analyses of all parameters with extrapolation to low doses of mercury and 6) risk assessment for adults and children depending on genotype, content of mercury in biosubstrata as well as water, food stuffs, air and soil and influence of socio-economic and psychological factors, taking into consideration results of the analyses of total mutagenicity of the environmental components. The obtained data will allow to select reliably people at lower risk for employment in the mercury industry, become a basis for a substantiation of new hygienic rules, will allow better estimation of the risk of mercury exposure and will also allow estimation of a potential risk for future generations.

The same approach might be fruitful for study individual effects of mercury and its compounds among indigenous populations in Northern Canada, Russia and other northern countries – what is in agreement with suggestions of colleagues from Canada.

Specificity of Diagnostics and Examination of Mercury Exposures

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Mercury pertains to thiol poisons blocking sulfhydric (thiol) groups which provide activity of more than 50% of enzymes. Loss of many physico-chemical and biological properties of proteins results in disturbance of protein, carbohydrate, and lipid metabolism in the organism. Main targets of mercury selective toxicity are the following: specific epithelium of kidneys, liver, and intestine, and nerve cells. So, psychoneurological symptomatology, nephropathy, hepatopathy often prevail in manifestations of toxic effects.

Diagnosing of extensive mercury exposures does not cause difficulties. Diagnostication takes into account specific clinical symptom complex supported by results of laboratory (in particular, increased concentration of mercury in biological matrices) and instrumental examination, and also long-term period of service at harmful production.

It is more difficult to reveal consequences of human exposure to low doses of mercury. It is necessary to take into account capability of mercury to deposit in different organs (liver, kidneys, spleen, brain, and heart) and effect on the body periodically entering from depot into the blood flow. At that toxic effect of mercury has no specific symptoms and syndromes. It appears as functional disorders, common symptoms and signs of poor health which hardly permit clear diagnosing of chemical exposure. Along with general toxic action, mercury and its compounds cause gonadotoxic, embryotoxic, theratogenic, and mutagenic effects, i.e. delayed effects.

In this case, expert examination of mercury exposures is based on studying of ecological situation, data of epidemiological researches (with analysis of the toxicant effects on cardiovascular and nerve systems, system of sense organs, reproductive system), and also data of comprehensive clinical examination of selected groups with using of specific diagnostic techniques.

Results of investigation of mercury vapor content in hospitals

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The ground for investigation of children hospitals in Almaty city in 1996 was information about frequent incidents of breaking thermometers there, each of them is known to result in concentrations of mercury vapors in the air of rooms of about 60 m^3 which are dangerous for human health.

More than 100 rooms for medical procedures, games and other auxiliary services have been investigated. The measurements of mercury vapors content were done by highly qualified personnel with help of commercial mercury atomic absorptive analyzer AGP-1 (Russia) provided with a metrological control device. Obtained results proved anticipated anxiety. About 50 % of the rooms' area turned out to be polluted with mercury vapors concentration of which ranged from 1 to 5 sanitary norms ($MPC_{extreme}$ is equal to 300 ng/m^3). In some spots the mercury concentration was found to be tens and more times higher than $MPC_{extreme}$.

The data obtained have enabled to draw following conclusions:

1. Taking into account both high toxic hazard of mercury for sick children and medical personnel and the fact that there is similar problem of mercury pollution of children hospitals in other cities of Kazakhstan it is necessary to conduct purposeful investigation of children hospitals in cities and towns of oblast and regional scale of the Republic and produce a database on level of mercury pollution for undertaking proper hygiene and sanitary actions.

2. To arrange works to make complete withdrawal of mercury thermometers and other mercury based devices from their use as well as to compile and disseminate normative-methodical and other materials related to safety guidelines among medical personnel.

3. Allowing for the data on mercury pollutions of big cities of Russian Federation and experience on their elimination it is necessary to create Center on Mercury Hazard Abatement I Kazakhstan with all necessary material and technical equipment and attracting qualified specialists in the area of analytical chemistry of mercury.

Mercury Containing Waste as Source of Environment Pollution by Mercury: Hygienic Evaluation and Demercurization

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The global character of environment pollution by mercury is determined by totality of physical-chemical, geochemical, industrial-engineering and medicobiologic properties, which are intrinsical to mercury, its organic and inorganic compounds. This fact generates a need to coordinate efforts of different countries and international nature-conservative institutions towards prophylaxis of mercurialism. It is necessary to bear in mind the specific character of environment pollution by mercury, which arrives from primary and secondary sources.

Systematic mercury (its compounds) displacement from circulation and reduction of its manufacture and trade for the reasons given above resulted in the fact that environment pollution level (emission in air, subsoil waters, ponds and soil) was determined to a greater extent by sources of secondary pollution such as mercury containing industrial waste, mercury polluted building and construction elements, furniture and equipment. Hygienic evaluation of the waste as potential source of environment pollution by mercury is determined by its mass, chemical formula of mercury in waste, aggregative state of waste, location of waste formation with respect to residential areas.

Demercurization effect consists in full or partial mercury extraction from waste, decrease of mercury solubility and/or volatility (its compounds) in waste. Evaluation of effectiveness and safety of demercurization of mercury containing waste as a technological process and its results is based on the totality of ecological, hygienic, ecologo-hygienic, economic, technological and designed-planned indices.

The peculiarities of waste luminescent lamps as a source of secondary mercury pollution and demercurization object are examined. A problem of pollution by mercury of technological equipment for chlorine and alkali production by mercurial method is studied as well as effectiveness of its demercurization, formation of sources of indoors air pollution by mercury, depot classification of mercury sorbed by structural elements of buildings. Scope of work and type of demercurization at the sorbed mercury contaminated structural elements of buildings are recommended.

Risk to residents living near the mercury pollution at Temirtau

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The study assessed the potential risk of the adverse health effects on the population living in the neighborhood of the mercury-polluted chemical factory in Temirtau. A dietary survey was carried out with the help of personal details and food frequency questionnaires, and hair samples were collected from residents of Temirtau and four riverine villages (Chkolova, Gagarinskoe, Samarkand, and Rostovka) to establish mercury levels. Fish from both markets and the River Nura were collected as well as samples of vegetables and meat to determine mercury contents. The result indicated that mercury concentrations in local people's hair had a mean of 0.577 μg/g but ranged from 0.009 to 5.184 μg/g. There were 12.9% of the hair samples exceeding 1 μg/g, corresponding to the reference dose (RfD) of 0.1 μg/kg bw/day by the US Environmental Protection Agency (US EPA). Most of the higher levels' samples were in downstream village of Rostovka (mean = 1.244 μg/g). Significant differences in concentrations of hair mercury were found between the following subgroups: mercury levels in males' hair were higher than females (0.825 and 0.416 μg/g); younger people, aged below 45 years old had less mercury concentrations than elderly people (0.462 and 0.777 μg/g); fish eaters accumulated more Hg than non-fish eaters (0.101 and 0.610 μg/g). A weak but significant correlation was established between hair mercury concentrations and fish consumption frequency (r = 0.197). Eating fish from the contaminated river or lakes accounted for a large proportion of mercury in human bodies as the mercury levels in river fish was found while approximately 10-fold higher than that in commercial fish. A Monte Carlo simulation of the data obtained from questionnaires provided a mercury distribution in the population that was closely correlated with that obtained in the hair samples. It can be concluded that despite the high levels of mercury in the sediments and fish, the average concentration in the population as a whole is not considerably high. There is 13% that have elevated levels that are not considered highly dangerous but undesirable.

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(Names of organizers and participants of the workshop are marked in thick type and co-authors of abstracts and presentation – in standard type)

Workshop Resolution

The international workshop has brought together 42 participants from: Kazakhstan, Russia, Canada,and United Kingdom. There were scientists, experts, decision makers of both local and national levels, specialists on decrease and management of risks posed by mercury contamination among the participants. The workshop was arranged and held by BG Chair of Environmental Technology of Almaty Institute of Power Engineering and Telecommunications and Climate Change Coordination Centre at financial support of ISTC as well as Ministry of Environmental Protection of the Republic of Kazakhstan and Department of Foreign Affairs and International Trade, Canada.

May 28
Pavlodar City

The participants of the workshop visited the site of mercury contamination at Northern industrial area of Pavlodar and were provided with information about implementation of the first phase of the Project of Demercurization of Chlor-Alkali Production at the former PO "Khimprom", Pavlodar. There was discussion of environmental problems of Pavlodar region and plans to continue works on cleaning the mercury contamination at Pavlodar Oblast Territorial Department of Environmental Protection.

The workshop participants and representatives of Pavlodar Oblast Territorial Department of Environmental Protection noticed the depth of investigation of the problems of the mercury contamination, wide involvement of public and mass media in their discussion as well as large scale and high quality of conducted researches and works on cleaning and containing main sources of the mercury contamination.

May 29
Ekibastuz City

The workshop participants visited a coal open-pit mine at Ekibastuz coal field (coal open-pit mine "Bogatyr'" belonging to Bogatyr Access Komir Company) and AES Ekibastuz Power Station (former Ekibastuz GRES-1). They got acquainted with current business as well as plans of the company on expansion of the production and environmental protection.

May 30
Astana City

In the first day of the workshop holding at the Conference Hall of "Akku" Hotel the participants were welcomed by: Mr. Kanat Baigarin - Head of BG Chair of Environmental Technology, Almaty Institute of Power

Engineering, Director of Climate Change Coordination Centre, Kazakhstan; Mr. Zeinulla Sarsembaev – Vise Minister of Environmental Protection of the Republic of Kazakhstan; Mrs. Nikola Kim - Program officer, Department of Foreign Affairs and International Trade, Canada; and Valentina Rudneva - Senior Project Manager, International Science and Technology Center, Russia, who summarized the experience and noticed the importance of international and regional cooperation in the area of minimization of mercury hazard.

Special session was devoted to ***Remediation of mercury contaminated territories*** both in Kazakhstan, Canada and Western Europe.

May 31
Astana City

The second day of the workshop was devoted to discussion of ***Mercury emissions to atmosphere and its global transport*** and possible cooperation of Kazakstani, Russian and Canadian scientists within ISTC in the different areas of mercury contamination problem. The workshop participants also visited the area of new buildings project in the new capital of Kazakhstan.

June 1
Astana City

The third day of the workshop was devoted to discussion of ***Risk assessment and mercury impact on health of population.***

In the framework of the workshop activity in its third day meeting of Mr. Farhad Kuanganov, Vice Minister of Science and Education of the Republic of Kazakhstan with Mrs. Nikola Kim and Mr. Kanat Baigarin took place. At the meetings the problems of searching schemes of cooperation of Kazakhstan with Global Partnership Program of Department of Foreign Affairs and International Trade, Canada were discussed.

The scope of the Workshop included the following activities:

1. There were made 23 presentations on different problems of mercury pollution interaction with environment and mercury effect on human health. All presentations were very interesting and topical from the point of view of scientists from Kazakhstan and Russian Federation as well as Canada.

2. Measures undertaken on constraining mercury contamination spreading in Pavlodar, which have no analogues in CIS, were recognized as highly valuable. There was provided information on the progress of the Nura River Clean-up Project and engineering solutions to be implemented whiles the project carrying out.

It was taken into consideration that since the project beginning public of Temirtau City have been kept informed continually about plans on the clean up from mercury in Temirtau in accordance with international and Kazakstani norms. Besides contractors conducting the work clearly understand difficulties of implementation of demercurization in the vicinity of the residential area and in the river's floodplain. Water Resources Committee of the Ministry of Agriculture of the Republic of Kazakhstan (WRC) provided information about the first phase of medical and ecological study conducted in cooperation by Worldwide Organization of Public Health, Ministry of Public Health of the Republic of Kazakhstan and WRC as well as information about interaction of WRC with Minamata Institute (Japan).

The workshop participants have suggested that clean-up activities in the Northern Industrial area of Pavlodar should be continued in terms of topsoil clean-up from mercury and decrease of risks posed by mercury contamination of the Balkyldak wastewater storage pond and groundwater which are still very high. Besides cleaning activities in both Pavlodar and Temirtau should continue to be accompanied by study of mercury contamination effects not only on the environment but also on human health.

3. As a result of discussions there were outlined new directions which could be basis for future projects in the area of different aspects of mercury contamination effects first of all human health effects and mercury emission to atmosphere.

4. There were developed 9 pre-proposals on new projects, which were delivered to the Canadian experts for discussing possible cooperation in the area of mercury hazard minimization. Detailed information on the pre-proposals will be sent to the Canadian experts within the next two months.

5. The workshop participants applied to the ISTC representatives of the Global Partnership Program (Canada) to consider the pre-proposals on the projects by October 2007 and to inform the ISTC what pre-proposals were selected. Then these pre-proposals will be further developed and applications for funding will be submitted to the ISTC according to the standard procedure.

C O N T E N T