SPECIFIC SUPPORT ACTION

BIOMERCURY

Worldwide remediation of mercury hazards through biotechnology

NMP2-CT-2004-505561

Priority 3 NMP: Nanotechnology and nanosciences, knowledge based multifunctional materials, new production processes and devices

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Period 3 Final Report

Period covered: *1/03/2004 – 28/02/2007*
Date of preparation: *June 2007*
Start date of project: *1.3.2004*
End date of project: *28.02.2007*
Duration: *36 months*

Project coordinator: Dr. I. Wagner-Döbler
Project coordinator organisation: GBF
New name since July 2006:
Helmholtz-Centre for Infection Research (HZI)

Publishable Executive Summary

Summary of project objectives

Mercury is a priority pollutant because of its extreme toxicity, global atmospheric transport and accumulation in the food chain. Removal of mercury from current industrial emissions as well as from previously polluted sites is therefore mandatory and should take into account the latest achievements in science and technology. A unique biotechnological process for removal of mercury from wastewater based on the enzymatic transformation reactions of live mercury resistant bacteria has been developed and operated in full industrial scale at a Czech chloralkali electrolysis factory. Another recent achievement are specially coated voltammetric electodes able to detect femtomolar amounts of mercury in a quick and simple way. These new technologies are environmentally friendly and cost effective and have a much broader potential than that realized to date, which, however, needs to be assessed carefully on a case by case basis for each new application. In the case of microbes, fundamental barriers of understanding and acceptance also must be overcome in order to promote their application. For full scale remediation, microbiological technologies have to be integrated into a complete process remediation scheme which also includes physical and chemical technologies, pre-treatment steps and waste disposal strategies.

The aim of the specific support action **BIOMERCURY** therefore is

- to evaluate the applicability of the new, microbe based technology, for clean-up of contaminated **air**, **wastewater**, **groundwater**, **soil**, **solid waste** from past industrial operations (e.g. electrolysis factory buildings), contaminated **rivers**, **lakes**, **swamps**, **coastal areas**, and **gold** and **mercury mines**, and **mine tailings**;
- to monitor the operation of the first **industrial microbe based mercury removal plant**, and to collect data on longterm performance;
- to **compare costs, safety and efficiency** of the new biotechnological approach to traditional methods;
- to **transfer knowledge** on the new biotechnological approach into countries were the problems are most urgent, e.g. Eastern and Southern Europe, Asia, South America and Africa;
- to coordinate activities and to **exchange information with US agencies** currently actively involved in implementing new control technologies, e.g. for coal fired power plants;
- to **communicate** relevant information to governments, decision makers and international agencies.

These goals shall be approached by an international consortium which will first conduct **case studies** on hot spots of pollution as well as on current mercury emitting industries. On this basis, **integrated engineering concepts** will be developed in cooperation with partners in affected countries. They will be communicated to Governments and International Agencies with the aim of implementing **demonstrations** or **full scale remediations.** Research

deficits will be identified in the process and will lead to new **R&D projects** within the European Community.

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Contractors

Part. Role *	**Part. No.**	**Participant name**	**Part.short name**	**Country**	**Date enter project**	**Date exit pro-ject**
CO	1	Helmholtz-Centre for Infection Research (formerly known as GBF)	GBF	Germany	1	36
CR	2	Technical University of Braunschweig	TUBS	Germany	1	36
CR	3	University of Southampton	SOTON	England	1	36
CR	4	Geotest	GEOTEST	Czech Republic	1	36
CR	5	Hebrew University of Jerusalem	HUJI	Israel	1	36
CR	6	Technical University of Lodz	TUL	Poland	1	36
CR	7	Jozef-Stefan-Institute	JSI	Slovenia	1	36
CR	8	University of Tirana	UT-LACH	Albania	1	36
CR	9	Almaty Institute of Power Engineering and Telecommunications	AIPET	Kazakhstan	1	36
CR	10	University of Cartagena	UC	Columbia	1	36
CR	11	Istituto de Ciências do Mar	LABOMAR	Brazil	1	36
CR	12	Rutgers University	RUTGERS	U.S.A.	1	36
CR	13	University of Florida	UF-COE	U.S.A.	1	36
CR	14	Environmental Protection Agency	EPA	U.S.A.	1	36

*CO = Coordinator
CR = Contractor

Work performed

1. Case studies

The BIOMERCURY project conducted five interdisciplinary case studies which covered hot spots of mercury pollution from former industrial activities in need of remediation, as well as current mercury emissions from industrial operations worldwide:

- Case study 1: Industrial Area Pavlodar, Kazhakstan
- Case study 2: Hot Spot of Pollution, Vlora, Albania
- Case study 3: Chloralkali Industry
- Case study 4: Coal Fired Power Plants and Municipal Waste Incinerators
- Case study 5: Oil and Gas Industry

Because of the special experience of contractors 10 and 11 (University of Cartagena, Columbia and Instituto de Ciências do Mar, Brazil) case study 1 was expanded to include

-Industrial Area North Coast of Columbia and Chloralkali Plant, Cartagena, Columbia

-Land use change and Hg remobilisation in the Amazon.

2.1. Compilation and evaluation of existing data, acquisition of missing data

Huge amounts of analytical data have previously been collected for some of the polluted sites, e.g. the Pavlodar Industrial Area, Kazhakstan (case study 1), and the Hot Spot of Pollution in Vlora, Albania (case study 2). In the course of the Biomercury project, these data were compiled and evaluated. Since mercury resistant bacteria can only detoxify ionic mercury, new samples were obtained and the concentration of ionic mercury was determined. Moreover, the concentration of methyl mercury compounds is the key to assess the danger of food chain accumulation and was therefore determined for selected samples, as well as the mercury concentration in hair and urine of humans living on the polluted factory sites.

For case study 3 (chloralkali electrolysis), a special measurement campaign was conducted in cooperation with the Electrolysis Factory Tarnow, Poland, who wishes to implement the microbiological wastewater treatment method. To design the biotreatment process correctly, daily fluctuations in mercury concentrations of the factory wastewater were determined for one month.

A completely different situation was encountered for current industrial emissions, e.g. coal fired power plants and municipal waste incinerators (case study 4) and oil and gas industries (case study 4). Published data are sparse, and since the analysis of very small concentrations of mercury in complex media like oil and gas is far from trivial, the available data must be treated with caution. Moreover, usually only global mercury balances are reported, while it is almost impossible to obtain actual concentration values for mercury in process waste water or scrubber solutions. Data on mercury speciation in these samples are almost completely lacking. To improve this situation, samples were obtained from some companies (Great Britain, Slovenia, USA, Germany) under strict secrecy agreements. A questionnaire was sent to coal fired power plants in Great Britain. However, only a preliminary assessment of the mercury pollution problem in these industries was possible in the frame of the current study.

2.2. Treatability studies with selected samples

Treatability studies were conducted for samples from case studies 1 – 4. No suitable samples could be obtained for case study 5 (oil and gas industry).

- Lake sediment from the Industrial area of Pavlodar (Case study 1)
- Process water from a soil washing plant in Vlora, Albania (Case study 2)
- Chloralkali factory wastewater from Tarnow, Poland (Case study 3)
- Mixed factory waste water from a chemical factory (Case study 4)
- Scrubber wastewater from a pilot waste incineration plant (Case study 4)

The microbiological process requires ionic mercury in ppm amounts to be efficient. Therefore, in the case of lake sediment and soil wash water treatment by mercury resistant bacteria was not possible because the mercury present was elemental mercury or bound to sediment particles and thus not biologically available.

However, all industrial waste water samples containing ppm amounts of ionic mercury which were tested could efficiently be cleaned by mercury resistant microorganisms. Experiments were successfully conducted on ***chloralkali electrolysis wastewater*** from a Polish factory (ZA Tarnow). The performance of the bioreactor was improved by using activated carbon as a solid support material for biofilm growth. Water from the ***waste air scrubber*** of the waste incineration plant Tamara and ***mixed wastewater from a chemical factory*** was also efficiently cleaned by bacteria. The latter wastewater contained ionic mercury in concentrations up to 150 mg/l, depending on the primary source (chloralkali electrolysis or waste incineration). Prior to microbiological treatment a dilution step is necessary because mercury concentrations above 10 mg/l are toxic even to mercury resistant microbes. In technical scale, this can easily be realised by recirculating a part of the effluent of the plant into the inflow.

2.3. Complete assessment of pollution problem, comparison of clean-up alternatives

An assessment of the total pollution problem was conducted in each case study. The total costs of microbiological treatment, including pre-treatment and final deposition of mercury containing waste, investment costs and running costs, were determined for chloralkali waste water based on the operation of the pilot plant at ECI Ibbenbüren, and compared to those of ion exchange columns, which are the best available alternative technology to date, and to hydrazine precipitation, the current treatment used by ZA Tarnow, Poland. A cost comparison was also conducted for chemical precipitation of heavy metals from scrubber waster water of a waste incineration plant in comparison to microbiological mercury removal.

2. Technology Transfer and Industrial Application

Technology transfer was mainly promoted by regular project meetings and by organization of two specialised workshops:

1. Chloralkali electrolysis industry (Lodz, Poland)
2. Vlora hot spot of pollution (Tirana, Albania)

As a result, a Polish electrolysis company (ZA Tarnow) decided to operate the microbiological treatment method. A grant was successfully obtained by Prof. Ledakovicz and Dr. Gluszcz from the Polish government for this purpose. HZI is supporting this project by consulting, bacterial strains and technical equipment.

A detailed description of the microbiological treatment technology was submitted to the European IPPC Bureau (www.jrc.es; http://eippcb.jrc.es). It will be taken into account in the review of BREFs, in particular for the review of the BREF on Chlor-Alkali (CAK), Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW) and Waste Treatments (WT).

Two other grant proposals were submitted in relation to the Biomercury project, one between Geotest Brno, Czech Republic, and Almaty Institute of Power Engineering and Telecommunications, Kazhakstan, which is pending, and one for a Humboldt-Fellowship for Prof. Jesus Olivero-Verbel, University of Cartagena, Columbis, which has been approved by the German Humboldt-Foundation and is due to start in March 2008.

Fig. 1. Meeting of Biomercury contractors with employees of Polish Zakłady Azotowe Tarnów S.A. (Nitrogen Company) in Tarnow, Poland, to discuss the possibility of a pilot operation.
From left to right: Dr. I. Wagner-Döbler, Mrs. Irena Janiszewska, Mrs. Katarzyna Zakrzevska, Dr. P. Gluszcz, Mr. Wojcieck Laleewicz, Prof. S. Ledakovicz.

The Biomercury consortium organized the following specialised meetings:

1. A bioremediation session at the **7th Int. Conf. On Mercury as a Global Pollutant,** June 2004, Ljubljana, Slovenia, organized by JSI.
2. **Workshop for Chloralkali Companies**, Technical University of Lodz, Poland, December 2004, organized by TUL.
3. **Workshop on Vlora Hot Spot of Pollution**, University of Tirana, Albania, April 2005, organized by TU-LACH.
4. **Biomercury Midterm Assessment Meeting**, GBF, Braunschweig, Germany, September 2005, organized by GBF.
5. **Project meeting in Prague**, Czech Republic, April 2006, organized by Geotest.
6. **Final project meeting in Southampton**, England, February 2007, organized by SOTON.

3. Reference to website

The Biomercury website can be found at

www.biomercury.de

Section 1 Project Objectives And Major Achievements during the Reporting Period

Overview of general project objectives

Introduction - general description and milestones

Toxicity of mercury. Mercury is the most toxic of all elements (Nies 1999)[1]. It has no beneficial biological function. In the environment, it can be transformed to methylmercury, which penetrates living cells within seconds and subsequently accumulates via the food chain, reaching high concentrations in its final components, e.g. birds of prey or fish. The main danger for humans lies in the consumption of mercury contaminated seafood. This route of exposure is of particular importance for pregnant women, and for women of child-bearing age in general[2]. Because of the global transport of gaseous elemental mercury, with a residence time in the atmosphere of about 2 years and possible precipitation in remote, pristine areas, the problem of mercury pollution needs to be addressed on a global scale.

Mercury pollution of the environment. In Europe and the US, the main user of mercury is the chloralkali electrolysis industry, with about 55 factories in Western Europe alone (European Commission 2000)[3]. About 1000 tons of mercury were supplied in the U.S. in 1995 and were used for the chloralkali industry and for manufacturing of electronic equipment. Although chloralkali plants are now phased out in Europe, the contamination they leave behind will still have to be dealt with. Moreover, Eastern European plants have to find cost effective solutions to reduce their emissions to European standards for the remaining operating time of 5 – 15 years.

Total mercury emissions in 1995 were estimated as 338 tons in Europe and 154 tons in the US, of which 136 tons were emissions to air by low level combustion sources, e.g. fossil fuels (coal, oil, gas), and waste incineration. Reduction of low level mercury emissions to air is therefore a high priority, both in the EU and the US (EPA 1997; EPA 2000)[4]. To obtain this goal in a cost effective way is a technically difficult task.

In Eastern Europe and worldwide, quantitative estimates are not available. However, in addition to ongoing industrial operations emitting mercury, many factory sites have been abandoned and are massively polluting soil, groundwater, lakes, rivers, and the seashore. Mercury mines and artisanal gold mining cause ecological problems and represent serious health risks

1 Nies DH (1999) Microbial heavy-metal resistance. Appl. Microbiol. Biotechnol. 51:730-750
2 Schrope, M (2001) US to take temperature of mercury threat. Nature 409:124
3 European Commission (2000) Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry. Integrated Pollution Prevention and Control (IPPC). World Trade Center, Isla de la Cartuja s/n, E-41092 Seville, Spain.
4 EPA (1997) Locating and estimating air emissions from sources of mercury and mercury compounds. EPA-454/R-97-012. Research Triangle Park, NC 27711, U.S.Environmental Protection Agency.
EPA (2000) Mercury Research Strategy. EPA/600/R-00/073. Cincinnati, OH 45268, U.S.Environmental Protection Agency.

for the people in the area[5]. Case studies included in this project are sites in Kazakhstan and in Vlore, Albania, which has been identified as a hot spot of pollution by the UNEP (Report 2000)[6].
Anthropogenically elevated Hg deposition in arctic and subarctic ecosystems is an emerging potentially serious environmental problem, particularly in Northern Europe and North America.

Currently used clean-up technologies. The best available technology for cleaning of mercury contaminated soil and sediment is thermal desorption at high mercury concentrations, and storage on landfills or in underground storage sites at low concentrations. To reach the European wastewater discharge limit for mercury (50 µg L^{-1}), the process effluent from chloralkali factories is cleaned by hydrogen sulfide precipitation, hydrazine precipitation or ion exchange columns (European Commission 2000)[1]. Clean-up of mercury contaminated groundwater is performed by filtering it through activated carbon either in situ (barriers) or ex situ (Means & Hinchee 1994)[7]. Waste air cleaning is currently not directed at mercury elimination. Some technologies removing sulphate and nitrate use wet scrubbers, which simultaneously remove some of the mercury from the waste air. However, gaseous emissions are difficult to control and typically about 25% of Hg entering power stations in coal is emitted as gaseous mercury in flue gases to the air.8 Although each of these technologies has severe drawbacks, including high costs, microbial technologies are presently not in use for ongoing industrial operations and restricted to bench scale or pilot scale work for remediation of polluted environments.

Microbial treatment. A novel biotechnology for clean-up of mercury polluted waste water based on a microbial detoxification mechanism has been developed, demonstrated and put into industrial practice at a chloralkali electrolysis factory by the GBF in cooperation with industrial partners[9]. It was shown to be efficient, simple, environmentally friendly and cost effective (website at **http://www.gbf.de/mercury_remediation1/index.html**). The objective of the present project is to explore the applicability of this technology to other types of mercury contaminated waste water and to develop new integrated engineering solutions for selected industrial applications. Although the microbial process is well characterized and the necessary conditions for its operations known, new types of wastewater need to be analysed carefully and their treatability be determined experimentally to exclude the presence of inhibitory compounds or toxicants which may be hard to detect by analytical chemistry.

Structure of the Workplan

The core of the project are interdisciplinary case studies. They are led by a participant who is particularly knowledgable for this field. Case studies will be conducted for important

5 Ebinghaus, R., Turner, RR, Lacerda, LD and Salomons, W. (1999) Mercury contaminated sites. Springer Verlag, Berlin.
6 Post-Conflict Environmental Assessment – Albania (2000). United Nations Environment Programme (UNEP), PO Box 30552, Nairobi, Kenya. http://www.unep.org
7 Means JL, Hinchee RE (1994) Emerging Technology for Bioremediation of Metals. Lewis Publishers, Boca Raton, Florida
8 Meij, R., Vredenbregt, L.H.J. and H.T. Winkel (2002) The fate and behaviour of mercury in coal-fired power plants. J. Air Waste Manage. Assoc. 52(8): 912-917.
9 Wagner-Dobler I, H.F.von Canstein, Li Y, Timmis KN, Deckwer WD (2000) Removal of mercury from chemical wastewater by microorganisms in technical scale. Environ. Sci. Techn. 34:4628-4634

mercury emitting industries (chloralkali industry, coal fired power plants, oil and gas industry) or polluted sites in need of remediation (Vlora, Albania; Kazakhstan industrial area). They will proceed in three stages:

1. Compilation and evaluation of existing data, identification of gaps of knowledge
2. Acquisition of missing data
3. Complete assessment of pollution problem, comparison of clean-up alternatives (effectiveness, environmental impact, costs).

Case studies will be followed by the development of an integrated engineering concept in such cases where microbiological treatment is applicable. The strength of the research and technology infrastructure present in the country where the mercury problem is located will be relied on to develop an integrated remediation strategy. This might be through monitoring of pollutant concentrations, setting up and monitoring of the microbiological treatment under the guidance of GBF, or construction and operation of engineering facilities required in the process. In such a way, the overall costs of remediation will be kept as low as possible. Moreover, the research infrastructure and responsibility of the participating countries will be strengthened.

The outcome of the case studies will be presented in various forms and for various audiences, e.g. written technical report, mercury website, special session on the Int. Conf. on Mercury as a Global Pollutant (Ljubljana, June/July 2004), targeted information events for key international bodies. The final goal (milestone) will be one or several of the following:

- Research project funded by EU or National Research Agency
- Demonstration project
- Full scale remediation or implementation of biotechnology

Objectives for the reporting period, work performed, contractors involved and main achievements

Objectives for the reporting period

In the first reporting period,

all case studies went through the first two stages described above:

1. Compilation and evaluation of existing data, identification of gaps of knowledge
2. Acquisition of missing data

In the second reporting period,

3. data were critically evaluated. This resulted in very different conclusions for the various case studies, which are given in more detail below.

4. Treatability studies were performed for appropriate selected samples with mercury resistant microorganisms in laboratory reactors.

In the third and final project year,

a complete assessment of the pollution problem, including a comparison of clean-up alternatives (effectiveness, environmental impact, costs) was provided for each case study. Final case study reports were provided. For these final case study reports a common format was adopted if it was possible.

Work performed and contractors involved

- Compilation of available data on mercury pollution (all partners)
- Transfer of information between partners (all partners)
- Field trips to acquire missing data (TUL, AIPET, UT-LACH, GEOTEST, UC, LABOMAR)
- Questionaire to acquire missing data (SOTON)
- Aquisition of samples from industries (GBF, TU-BS, SOTON, Geotest, TUL, JSI)
- Analysis of samples (GBF, TU-BS, TUL, JSI, AIPET, UT-LACH, HUJI, GEOTEST, UC, LABOMAR)
- Microbiological investigations (TU-BS, GBF, TUL)
- Biochemical engineering investigations (TU-BS, GBF, TUL)
- Organization of specialised meetings and project meetings (GBF, UT-LACH)
- Participation in meetings and conferences (all partners)
- Maintenance and update of **Biomercury** website (GBF)
- Construction of database of chloralkali companies (TUL)
- Construction of website for Pavlodar site (AIPET)
- Planning of pilot operation at Tarnow (TUL)
- Networking with national and international agencies (all partners)
- Application for follow-up projects (Geotest, TUL, AIPET)

Main achievements

All deliverables which were due until month 36 have been provided.

Additional work has been conducted in the form of case studies on sites which were not originally included in the proposal:

D39 Industrial Area North Coast of Columbia and Chloralkali Plant, Cartagena, Columbia (UC).

D40 Land use change and Hg remobilisation in the Amazon (LABOMAR)

A pilot operation at the chloralkali factory in Tarnow is planned by TUL in cooperation with HZI. A grant by the Polish Government was obtained for this purpose by Prof. Ledakovicz and Dr. Pawel Gluzcz.

A Humboldt-Fellowship was obtained by Prof. Olivero-Verbel, UC, Columbia, from the German Humboldt-Foundation for a 1-year research grant at the laboratory of Prof. Wagner-Döbler, HZI, Braunschweig.

The microbiological remediation technology was submitted to the European IPPC Bureau for for inclusion into the document on Best Available Technologies in the area of (1) Chlorakali wastewater, (2) Common Waste Water and Waste Gas Treatment /Management Systems in the Chemical Sector, and (3) Waste Treatment. The submitted document was included as an additional deliverable (D41) in this report:

D41 Best Available Technology

Section 2 Workpackage Progress of Period 3

Work Package 1: Industrial Area Pavlodar, Kazakhstan

Objectives and starting point

Mercury pollution in Pavlodar is caused by an abandoned chloralkali plant. Whilst a lot of data has already been gathered to assess the risks, the mercury concentrations currently remaining in the groundwater, lake water, sediments and soils at the Pavlodar site are still an unsolved problem for which cost-effective remediation options must be found.

The initial plans for WP1 included:

- Gathering and critical evaluation of existing data on mercury pollution of soils, sediments, groundwater, surface water, air and fish at and around Pavlodar Chemical Plant (PCP);
- Identification of data gaps and conduction of small-scale targeted fieldworks campaign for acquiring of missing data;
- Compilation of database on mercury pollution at the Pavlodar site;
- Discussion of potential clean-up options and their evaluation in terms of effectiveness, environmental impact and feasibility/cost;
- Sampling of groundwater and sediments for subsequent feasibility study using microbiological methods.

Progress towards objectives

All objectives were met in a cooperation between AIPET (the work package leader), GBF, TU-BS, SOTON and GEOTEST. In addition to deliverables D1 and D2, which were due in February 2005, a treatability study was conducted by TU-BS to determine if mercury could be removed from lake sediments by mercury resistant bacteria.

A final case study report was provided which includes all work that has been done on the Pavlodar Chemical Factory site, the decision process towards the remediation, the full scale remediation work and a proposal for follow-up monitoring studies.

Work carried out by AIPET

The work package leader is **AIPET.** Starting date of AIPET´s activities on WP1 was March 2004.

During the reporting period the following activities within WP1 were performed:

1.1.1 Field works

1.1.1.1. Investigation of groundwater

Groundwater investigation has been carried out in places of mercury contamination with purpose to receive the data on total and methyl mercury concentration changes.

1.1.1.2. Groundwater sampling for their analysis for total and methyl mercury

Groundwater samples were being taken from 87 observation boreholes of the system of mercury monitoring at the Northern industrial area of Pavlodar using a submerged electrical pump in June and July, 2006 according to the technique developed by AIPET in 2001-2002. Simultaneously with groundwater sampling measurements of water surface, temperature and pH were taken.
Groundwater samples for methyl mercury determination were taken in duplicate from three boreholes C69-02, C32-03 and P8 on the 21st of July, 2006 following the same method as that for total mercury. The difference was that water samples for analyses for methyl mercury were taken into 1 liter one-use vodka glass bottles closed with metal screw-tops having plastic cover gaskets. The bottles were washed first with bromite-bramate mixture (see in Section 8.2.2) and then a few times with reagent water. The bottles were put an icebox immediately after their filling up with water samples and delivered to the analytical laboratory of Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia. During stops on the way the samples were kept at the temperature of 4°C in stationary refrigerators. The samples were delivered to the laboratory on the 4th of August, 2006 and kept at 4°C in a fridge until being processed. Also two empty bottles washed with the same way were sent to the same laboratory as blanks.

1.1.1.3. Investigation of soil mercury contamination

Investigation of soil mercury contamination was conducted on the site in 2002-2004 to assess the possibility of capillary rise of mercury into the pasture.

1.1.1.4. Investigation of mercury contamination of soil at the industrial area of the former chlor-alkali production plant.

19 soil samples were taken at the industrial area of the former chlor-alkali production and in the area of former 6th wastewater pumping station in July of 2006. The samples were taken in places of intensive mercury pollution (the map of mercury pollution with results of monitoring of 2001-2002 was used) from topsoil (0-10 cm) into duple one-use plastic bags. Also efficiency of demercurization works at the industrial area of former chlor-alkali production, at the area of former 6th wastewater pumping station and special storage ponds for solid and liquid mercury wastes was estimated with help of analysis of near-earth air (10 cm of ground surface) in 20 points for mercury vapors content. The measurements were implemented on the 21st July, 2006 since 3 pm till 6 pm at the air temperature of 27°C in cooperation with specialists from AO GEOtestBRNO (Brno, Czechia) using portable mercury atomic absorptive spectrophotometer (AAS) Lyumex RA 915+ (Russia)

1.1.1.5. Investigation of mercury pollution of Lake Balkyldak

Investigation of mercury pollution of wastewater storage pond - Lake Balkyldak included investigation of bottom sediments of the Lake.

1.1.1.6. Estimation of mercury pollution in bottom sediments of Lake Balkyldak

Beforehand four variants of sampling plan for 200, 150, 100 and 50 sampling points of wastewater storage pond Balkyldak bottom sediment were prepared on a regular grid using GIS of the Northern industrial area of Pavlodar so that it could be possible to choose the optimal one to follow to in situ depending on complexity and timing of field work carrying out.

Winter field works was conducted in March 2006 when the air temperatures had risen to –10^{o}C. These works was interrupted at the end of March after the ice started cracking when the temperature had risen above 0^{o}C. In the winter of 2005/2006 the ice thickness on Lake Balkyldak reached 0.6 – 0.9 m. allowing cars to move across the surface (the area of about 23 km^2) of the lake. However snowdrifts made the field works very difficult in the reed thickets. During a month of field works we managed to realize with little excess the regular sampling plan for 50 sampling points (excluding sampling points where it was impossible to take bottom sediments because of ice reaching the bottom; such samples were taken in summer time). In total 107 bottom sediment samples have been taken from 52 sampling points through the holes drilled through the ice with help of samplers of two different constructions: soft sediments were taken layerwise at 50 cm intervals, clay samples were taken from surface bottom layer to the depth of 25 cm. Using the samplers it was possible to take ground at pond's depths down to 12 m (bathymetric and soft sediment capacity measurements were being done simultaneously with sampling). Coordinates of sampling points were determined with help of hand-held GPS with maximum error of 7 m.
Summer bottom sediment sampling was conducted in July 2006. 33 samples from 17 shallow sampling points located near the shoreline of Balkyldak. The samples were taken from a boat board into tagged double plastic bags similar to the winter sampling (bottom sediment sampling far from the shore was impeded due to strong waving and the equipment bulkiness).
Measurements of soft sediments thickness were carried out simultaneously with bottom sediment sampling.

1.1.2.1. Chemical analytical

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

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

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

1.1.3.1. Office study

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

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

1.1.3.1.2. Analysis of the results of investigation of groundwater mercury contamination.

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

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

1.1.3.1.3. Analysis of the results of investigation of soil mercury contamination.

The results of determination of mercury concentration in soil samples taken within the industrial area of former chlor-alkali production and in site of 6th wastewater pumping station have shown that in general soil mercury contamination levels close to the plant are still high (from 2.1 to 95.1 mg/kg at maximum permissible concentration of mercury in soil - MPC_s being 2.1 mg/kg in Kazakhstan). At that some mercury concentrations can reach extreme values in the order of g/kg. Thus despite the initial clean up of the most contaminated area this indicates that a further clean up is required.

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.

Results showed a persistent high level of risk for personnel working near the site of the former chlor-alkali production plant and the insufficiency of the initial clean up measures. Persistent soil mercury contamination can in turn entail additional entrance of dissolved mercury into groundwater due to infiltration of atmospheric precipitation through the contaminated layer because this contamination extends beyond the area confined by the cut-off wall. All this necessitates carrying out more detailed investigation of mercury contaminated topsoil within the industrial area of the resulting in production of new map of the contamination (see Section 9).

Measured concentrations of mercury vapors which were about 200 ng/m^3 (on two measuring points) in the center of the landfill for building structures (50 m to the south from the former building 31) and from 100 to 200 ng/m^3 (on four measuring points) on site of special ponds for solid and liquid mercury waste located at south shore of wastewater storage pond Balkyldak proved quite good containment of the mercury waste by these engineering structures.

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

In April, 2006 and October, 2006 two scenarios of computer maps of depths and thicknesses of bottom sediments of Lake Balkyldak have been produced based on the data. The second scenario of the map (Fig.2, Annex 1) differs from the first one in an increase by 1/3 in number of depth and bottom sediment thickness measuring points (due to summer field works) and in using "Spline" method instead of "Inverse distance weighted (IDW)" method for interpolation (in the second case the picture on the bottom sediment thickness map correlated better with the picture on the bathymetric map.

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

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

Work carried out by GBF

The main input of participant 1 into this work package was into D2 (Feasibility study of selected samples) and was completed by the end of the first reporting period.

In 2005, GBF advised AIPET on the sampling methodology for methylmercury determination.

GBF considered several project proposals which AIPET suggested for future cooperation for mercury remediation in the Pavlodar area. However, there is almost no solved ionic Hg(II) present in any of the sites under consideration, and therefore the microbiological method is not applicable. Mercury in Pavlodar soils and in the sediments of Lake Balkyldak is present either as elemental mercury, or as complexed bound mercury which is not bioavalable.

Groundwater samples with low concentrations of ionic mercury were sent to participant 5 (HUJI) for testing the electrochemical electrodes developed by HUJI for mercury.

Work carried out by TU-BS

During the reporting period the following activities within WP1 were performed by TU-BS (contractor 2):

1. With Participant 9, AIPET, the situation in Kazakhstan was discussed. Gaps of measured mercury concentrations were found and a measurement of methyl mercury concentration was proposed.
2. Hot spots of mercury contaminated areas were identified (lake near Pavlodar) and it was proposed to investigate this area for a feasibility treatment with the biological process
3. Data acquisition was done and a brainstorming of a feasible process routes were discussed
4. Samples of contaminated soil were delivered by AIPET and investigated from the TU-BS. The aim was to get information about the speciation of mercury and the bioavailability of mercury for a further treatment. Until now it could be seen that a biological treatment is not possible (D2).

Work carried out by SOTON

Work on WP1 started in SOTON from March 2004. The results on mercury pollution at the Pavlodar site which were obtained within the framework of a previous EU funded project (Inco-Copernicus ICA2-CT-2000-10029) as well as other relevant background literature for the project was reviewed. The data was then prepared for oral presentation at the 7th International Conference on Mercury as a Global Pollutant in Ljubljana which took place in June-July 2004. Potential clean-up options for the site were subsequently discussed with the coordinator and other project participants whilst in Ljubljana. The project team concluded that the mercury-contaminated lake which is situated approximately 2 km north of the former chloralkali plant appears to pose a greater threat than the mercury-

contaminated groundwater, and might therefore be a better target for remediation efforts. It was agreed that Participant 9 would conduct further studies to fill data gaps, and that SOTON would provide data on current contamination status of the lake. This data was passed to the project coordinator at the following project meeting in Lodz, Poland, in December 2004. The remaining data on mercury pollution at the Pavlodar site was prepared and summarized in February 2005 and sent to Participant 9 and the project coordinator for inclusion in the database (deliverable D1).

Work carried out by UC

- Review and analysis of the existing data on mercury pollution at the North of Colombia. This included the main gold mining areas, their different influence zones, and the extinct chloroalkali plant located in Cartagena Bay.
- Due to the lack of information on mercury levels in humans living at the North Coast of Colombia, in particular along the coast line, this work included the sampling and analysis of mercury in hair of people living within and around Cartagena Bay, the most important industrial area at the North of Colombia.
- All gathered and compiled information has been added into a geographical information system.

Work carried out by LABOMAR

The starting date of LABOMAR's activities on WP1 was May 2004.
The initial plans for WP1 included:

- Optimising and calibrating a sampling and measurement package for the determination of Hg re-emitted by contaminated soils
- Compilation of database on mercury pollution at the Madeira River basin

During the reporting period the following activities within WP1 were performed:

1. Installing a controlled atmosphere environment to calibrate and optimize gaseous Hg determination under the conditions found in the Amazon region.
2. Determined analytical parameters of the equipment used
3. Optimize the sampling procedure using closed Teflon chamber
4. The results obtained during these experiments were compiled for presentation and discussion with the scientific communities at two major conferences on environmental chemistry

A review on the mercury contamination of the Madeira river Basin was compiled and submitted for publication in *Geochimica Brasiliensis*, journal of the Brazilian Society of Geochemistry ***(Bastos WR & Lacerda LD (2004) Mercúrio na Bacia de Drenagem do Rio Madeira, Rondônia. Geochimica Brasiliensis 18(2): in press.)***

List of deliverables for WP1

Del. no.	Deliverable name	WP no.	Date due	Actual/ Forecast delivery date	Lead contractor

D1	Database on mercury pollution at the Pavlodar site	1	Feb. 05	Feb. 05	9
D2	Fesaibility study of selected samples by biological method	1	Feb 06	Feb 05	2
D3	Case study report on Pavlodar site	1	Aug 06	Jan 07	9
D4	Symposium in Kazakhstan*)	1	Apr 06	Apr 06	9
D39	Industrial Area North Coast of Colombia and Chloralkali Plant, Cartagena, Columbia	1	Feb 02	Feb 02	10
D40	Land use change and Hg remobilisation in the Amazon	1	Feb 02	Feb 02	11

*) It was decided to cancel this meeting because of too high costs. The annual project meeting was held at Prague (18. – 20. May 2006) and organized by Geotest.

Work Package 2: Hot Spot of Pollution, Vlora, Albania

Objectives and starting point

Four miles north of Vlora in Albania is the site of a former chemical complex that produced chlorine alkali, vinyl chloride monomer and polyvinyl chloride. The plant was closed in 1992, and its buildings have been completely destroyed since that time. Families now live on and around the industrial site. The factory encompasses approximately one km^2 and is located directly on the Adriatic Sea. A major environmental problem is posed by the destroyed former chlorine-alkali electrolysis plant. UNEP observed drops of metallic mercury in the hall of the electrolysis plant and in all of its drainage canals. A UNEP soil sample found mercury levels > 10,000 mg/kg in the area of the former plant. This level is 1,000 times greater than typical EU thresholds. Between the former plant and the Sea is an area formerly used for the disposal of the factory's industrial wastes. It is likely to be highly polluted. The site was defined as a "hot spot of pollution" by a recent UNEP investigation.
The objective of this SSA is the precise evaluation of contamination levels and the reduction of the hazard of the contamination using a biotechnological process developed by GBF, through soil washing and subsequent microbial treatment.

Main objectives for the first and second project year are the following:

1. Gathering and critical evaluation of existing data on mercury pollution of soils, sediments, groundwater, surface water, air and biota at Vlora Hot Spot Pollution (the territory of ex-PVC Plant);
2. Identification of data gaps and conduction of small-scale targeted fieldworks campaign for acquiring of missing data;
3. Compilation of database on mercury pollution;
4. Monitory of contaminated level (analysis of different state of Hg by CV-AAS) in soils, sediments, seawater and biota samples

Progress towards objectives

Objectives were fully met by UT-LACH. In particular, D8 (Symposium in Albania) was organized by UT-LACH with great successs.
In addition to D5 (Report on Vlora pollution), a treatability study was conducted by TU-BS on a soil wash sample obtained from GEOTEST, thus D6 (Report on treatability study with microbiological method) had been provided 1 year ahead of time.
An updated and improved version of D5 was provided by UT-LACH in February 2006.

Work carried out by UT-LACH

The work package leader for WP2 is **UT-LACH**, and starting date of activities on WP2 was March 2004.

During the reporting period the following activities within WP2 were performed:

- Organization of the workshop on Vlora Hot Spot Pollution, Tirana (meeting in Tirana and trip in Vlora ex-Chlor Alkali Plant)
- oral presentation on actual mercury pollution at the Vlora ex-Chlor Alkali Plant site at the workshop on Vlora Hot Spot Pollution, Tirana
- Posters presentation (4 posters) at the workshop on Vlora Hot Spot Pollution, Tirana
- discussion of new situation of Vlora ex-Chlor Alkali Plant after the intervation from some companies having business activity on the area (midterm assesment meeting of the group)
- preparation of new data on contamination of Vlora ex-Chlor Alkali Plant using for data-base of mercury pollution at Vlora ex-Chlor Alkali Plant site (deliverable D5))
- gathered information on the history of Vlora ex-Chlor Alkali Plant, its operating technology, source of pollution during the operation period and after closed of the plant for inclusion in the report of Vlora site, aiming to complete assessment of pollution problem of this site (D7)
- review of the published literature
- oral presentation on actual situation on mercury pollution at Vlora ex-Chlor Alkali Plant site reported in Midterm Assessment Meeting, Biomercury, 14. – 15.9.2005, GBF, Braunschweig, Germany
- Poster presentation reported in Midterm Assessment Meeting, Biomercury, 14. – 15.9.2005, GBF, Braunschweig, Germany
- Updating the results of Hg content in soils before and after cleaning process (analysis of 12 soil samples)
- Updating the results of Hg content in hair samples of the children living inside territory of Vlora Hot Spot pollution (analysis of 22 hair samples), aiming to complete the data on mercury pollution of the Adriatic Sea as well as mercury concentrations in hair of people living on this site, the data which will be included in the final case study report
- Optimization of the analytical methods for the determination of Hg_{tot} in urine samples and Hg_{tot}, MeHg in fish and mussel samples.
- Preparing the intermediate report of Vlora Hot Spot pollution (50 pages)

Work carried out by GBF

A workshop was held in Tirana on 25.-28. April 2005 (see Biomercury website and WP 8) on the hot spot of pollution in Vlora, Albania. It included an extensive presentation of the microbiological method to the agencies, ministries, scientists and companies interested in the Vlora pollution.

The participants of the workshop visited Vlora on the next day and were informed by the former director of the chloralkali electrolysis plant about the extent of mercury pollution in the area. The soil cleaning technology installed by Geotest was demonstrated to us in operation, and Dr. Jaroslav Reif gave a presentation on mercury pollution in some Arab countries.

Attempts were also made to raise the interest of the German Embassy in Tirana, but unfortunately no appointment had been made ahead of time and so our small delegation, consisting of Geotest, TU Braunschweig and GBF, was rejected at the gate.

It was decided that UT-LACH should measure the samples taken by Geotest during the operation of the soil cleaning technology.

Work carried out by TU-BS

- Meeting in Albania (25 – 28. April 05)
- Explanation of the Operation of the Soil Wash Plant from GEOTEST
- Completion of the mercury mass balance
- Taking samples for Hg measurement and further remediation of the sludge from the sedimentation basin

Work carried out by GEOTEST

This work aimed at the development of an integrated soil wash technology including microbiological treatment and is described under WP 6 (Integrated Engineering Solutions).

Work carried out by JSI

Two water and five sediment/soil samples were received 28.11.2005 in 0.5 L glass bottles. Also the sediment/soil samples were received with very high water content. The samples were refrigerated at 4°C until further processing.

The samples were processed on 22.12.2005 and 28.2.2006 for total mercury analysis and on 19/ 20.1.2006 and 26/27.1.2006 for MeHg analysis using validated Standard Operating Procedures. Samples were analysed twice due to the inhomogeneity of the sample and consequently irreproducible analysis.
The results were sent to the GEOTEST (partner number 4.

List of deliverables for WP2

Del. no.	Deliverable name	Work-pack-age no.	Date due	Actual/ Forecast delivery date	Lead con-tractor
D5[1)]	Report on Vlora pollution	2	Feb. 05	Feb. 05/06	8
D6	Fesaibility study of selected samples by biological method	2	Feb 06	Feb 05	2
D7	Case study report on Vlora Hot Spot of Pollution	2	Aug 06	Oct 06	8
D8	Symposium in Albania on mercury pollution problems and solutions	8	Apr 05	Apr 05	8

Work package 3: Chloralkali Electrolysis Industry

Objectives and starting point

The chloralkali electrolysis industry is the biggest user of mercury. Even if mercury cell processes are phased out in the European Community, they are still operating in Eastern Europe and worldwide. Air and water emission have to be reduced to European standards in candidate and new member countries in an economically feasible way for the remaining operating time of at least 10 - 15 years.

The activities of the Consortium as an offerer of the know-how of the new technology of mercury bioremediation from chlor-alkali industrial wastewaters are aimed at:

- providing information on the novel mercury bioremediation technology to the end users (link to WP8);
- teaching potential users (companies using amalgam process, environmental officers, etc.) about implementation of the novel biotechnology,
- looking for improvements in microbial removal of mercury from the electrolysis wastewater (link to WP7) and developing new integrated engineering solutions for selected industrial applications.

Although the process of microbial reduction of mercury is well characterized new types of wastewater need to be analysed carefully and their treatability be determined experimentally to exclude the presence of inhibitory compounds or toxicants which may be hard to detect by analytical chemistry. Hence, in the reporting period the main task within WP3 was to perform experiments using microbiological method on chlor-alkali wastewater samples from electrolysis companies with different process characteristics.

Progress towards objectives

The objectives of the Biomercury project were completely accomplished. All work packages were provided. A grant proposal by TUL was approved by the Polish government to operate a microbiological pilot plant at ZA Tarnow, Poland. The microbiological wastewater treatment technology was submitted to the IPPC Bureau and is now under consideration.

Work carried out by TUL

1. Experiments on chloralkali wastewater samples from electrolysis companies

The experience gained during earlier operation of the instalation *bioMER* in Czech chlor-alkali company led to the idea, that the process of bioremediation may be integrated in one bioreactor with the sorption of mercury from wastewater, by immobilization of the microorganisms directly on the activated carbon. Such modification of the apparatus may increase efficiency of the technology and decrease the cost of the installation. As one of the goals of the WP3 is “looking for improvements in microbial removal of mercury from the electrolysis wastewater and to develop integrated engineering solutions”, the above men-

tioned modification of the bioreactor was applied in treatibility studies on chloralkali wastewater samples. However, for this experiments it was necessary to define several significant parameters of the activated carbon used and to investigate the Hg sorption process itself. Although the experimental work on activated carbons was not financed by BIOMERCURY project funds, it caused about five month delay in wastewater treatibility experiments within this project. Now these investigations are being performed (using wastewater of different characteristics from Polish chloralkali amalgam installations) and date of the results delivery is postponed to 31.07.2006.

2. Using and disseminating the knowledge

1. In order to disseminate information about the novel mercury bioremediation technology not only to chlor-alkali industry but also to broader group of potential users, the technology itself and experimental results dealing with its improvement were presented at two conferences. The following papers were presented:

- "Improvement of the mercury bioremediation method used for industrial wastewaters", at the Polish Conference "Progress in Bioreactor Engineering", Lodz, Poland, June 2005,
- and published in "Chemical Engineering and Equipment", **4**, 20-23, 2005 (in Polish);
- "Modification of the microbiological method for mercury remediation from industrial wastewater", at the 12th European Congress on Biotechnology, Copenhagen, Denmark, August 2005 (abstract in Journal of Biotechnology, vol 118, Supplement 1, 163, 2005).

2. From discussion with representatives of chlor-alkali industry it may be concluded that the main obstacle preventing broader application of the bioremediation technology in industry is the fact, that the method is not included in the Reference Document on Best Available Technique (BAT) in the Chlor-alkali Manufacturing Industry which have been published in 2000 by IPPC Bureau in Sevilla, hence the microbial method is not officially accepted in EU as a BAT. Taking this into account several relevant institutions were contacted, to gain the information about usual way of recommendation of a new technology to industry and about possibility and appropriate procedures for introduction of the bioremediation technology into the IPPC Reference Document in the future.

These were as follows:

- EIPPC Bureau in Sevilla, Spain (Mr. Luis Delgado, head of the bureau , and Mr. Elizeusz Karp);
- Polish Chamber of Chemical Industry (Dr. Ginter Nawrat, coordinator for chlor-alkali industry in Poland);
- "Responsible Care" Program (the pro-ecological initiative, implemented by world-wide chemical industry) (Mr. Jacek Różycki, head of the Polish bureau of the Program).

Contacts with above mentioned persons enabled dissemination of the information about BIOMERCURY project and technology, however by now we have received answer only from EIPPC Bureau from Sevilla (letter enclosed). The efforts will be continued.

3. Polish Zakłady Azotowe Tarnów S.A. (Nitrogen Company) in Tarnow, using amalgam chlor-alkali technology, was also contacted and the cooperation between Company and TUL in implementing the bioremediation technology in this factory was proposed. The NC Tarnow declared an interest in such colaboration, so further settlements will be discussed with them in the nearest future (April 2006). There is a possibility to apply for a grant to Polish Ministry of Education & Science for testing the microbial process in industrial scale in Nitrogen Company Tarnow, so relevant application for this is also being prepared.

Work carried out by GBF

GBF cooperated very closely with TUL to establish microbiological bioreactors and improve their performance by using activated carbon as support material. GBF provided mercury resistant strains, experimental protocols and day-to-day advise.

A Ph.d. student, Katarzyna Zakrzevska, worked at the GBF for several months under the supervision of Johannes Leonhäuser (TU-BS) and Irene Wagner-Döbler (GBF).

Contacts with the Polish electrolysis factory in Tarnow were strengthened by sending all available information material. Mrs. Zakrzevska visited Tarnow to obtain samples from electrolysis wastewater for bioreactor studies.

Tarnow expressed strong interest in setting up the microbiological technology to replace the old hydrazine treatment method, which does not meet European standards. Therefore, a delegation from TUL (Prof. Ledakovicz and Dr. Gluscz), TU-BS (Mr. Leonhäuser) and GBF (Dr. Wagner-Döbler, Mrs. Zakrzevska) visited Tarnow on 27th April 2006. The technology was presented by Dr. Wagner-Döbler to the director, Mr. Witold Szczypinski, and involved representatives of the company. The presentation was received with great interest, and the director agreed to cooperate in the frame of a grant which will was applied for by TUL. It was approved by the Polish government and started in March 2007.

Work carried out by TU-BS

- Provide instructions for microbiological experiments to the TUL so that they can do treatibility studies with activated carbon and the mercury resistant microbes
- Provide mercury resistant microbes to the TUL
- Supervision of member of TUL at the TUBS for operation of bioreactors with activated carbon as support material
- Meeting with a German chlor alkali factory. Provide information about the investment and operation costs for a full scale biological mercury removal plant. Calculation / pre construction of full scale pre-treatment unit.
- Treatibility study of wastewater from a German chlor alkali factory

Work carried out by AIPET

- First edition of article in Russian language have been prepared by V.Panichkin, M.Ilushchenko, L.Postolov "Forecast of distribution of mercury contamination outside of industrial area of JSV "Radical" Kiev city, and justification of net of ground water monitoring", describing current condition and forecast of distribution of mercury contamination of ground water toward to river Dnepr in Kiev city (30 pages). Mercury contamination of city territory appears due to industrial activity of local chlorine alkali industry in 1954 to 1996.
- In February 2006 web-site http://Hg-Kiev.narod.ru was opened, above article was placed there. For the current month more than 200 visitors had visited this site.

List of deliverables for work package 3

Del. No.	Deliverable name	WP no.	Date due	Actual delivery date	Lead contr. no.
D9	Database of companies using the chloralkali electrolysis process	3	Feb 2005	Feb 2005	6
D12	Meeting with chloralkali industries	8	Feb 2005	Dec 2004	6
D10	Assessment report on waste water clean-up alternatives	6	Aug 2006	Aug 2006	6
D11	Report on treatability study using microbiological method	6	Feb 2006	Jan 2007	6
D41	Microbial mercury remediation as Best Available Technology	3	Feb 2007	Feb 2007	3

Work package 4: Coal Fired Power Plants and Municipal Waste Incinerators

Objectives and starting point

Coal-fired power plants and municipal waste incinerators are the dominant sources of atmospheric mercury pollution world-wide. Emissions from combustion facilities depend on the chemical form of the mercury (Hg species) in the exhaust stream and the type of air pollution control equipment employed. Most mercury emitted from power plants is in the elemental form, which is difficult to control and is likely to enter the global atmospheric cycle. Oxidized mercury can be captured in scrubber liquids, from where it can be removed using microbiological processes. The objectives are

- to create a data base on mercury emissions from coal fired power plants and municipal waste incinerators;
- to establish the capabilities of existing and emerging control technologies;
- to evaluate the applicability of novel microbial technologies for the clean-up of mercury contaminated air;
- to identify gaps in the current knowledge and future research needs.

Progress towards objectives

All deliverables were successfully provided with little delay. Unfortunately, the available data on wastewater treatment of coal fired power plants and municipal waste incinerators are not sufficient for the purpose of the Biomercury project. Therefore, huge attempts were made to contact factories directly and to obtain data and samples. Because of the variability in wastewater treatment systems employed by the factories, no consistent picture is emerging yet with respect to the effectiveness of wet scrubbers for retention of mercury and their mercury concentrations. Most probably, we will have to focus on factories employing a highly acidid prescrubber.

Work carried out by SOTON

SOTON is leading case study 4. Progress on this work package was initially slower than expected, mainly because data collection proved to be more difficult than anticipated and little data was forthcoming from the other project participants. The database deliverable D13 was therefore finalised in June 2005 instead of March.

It became apparent that power stations would have to be approached directly for data. A questionnaire was designed and was sent out to all U.K. power stations in May once their exact contact details had been established (Appendix 1). Additional information received directly from U.K. power stations was incorporated in the database, and two stations agreed to provide samples. However, despite the initial agreement, follow-up letters had to be written and telephone calls made until samples were finally obtained several months later. Detailed instructions for sampling were sent to the plants and samples were collected in person after Materials Transfer Agreement was drawn up. These visits also provided an

opportunity for further discussions and to obtain detailed process schemes. Samples were sent out to GBF for analysis as soon as the signed Materials Transfer Agreement was received. Additional samples were analysed by SOTON who acquired a Millenium Merlin system for Hg analysis in January 2006. The analytical method was validated in February 2006 and power station samples were analysed (for the Analysis Report see Appendix 3). Any samples to be collected by SOTON in Year 3 of the project can be analysed directly in Southampton, and only samples with high enough concentrations for bioremediation experiments will need to be forwarded to GBF.

Many additional enquiries were made, e.g. to Fawley Power Station (an oil-fired power plant near Southampton - they do not have a scrubber), the new Municipal Waste Incinerator in Southampton (it has a dry scrubber, so it produces only solid waste), Didcot Power Station near Oxford (they do not have an FGD), Ratcliffe Power Station near Nottingham, a Municipal Waste Incinerator in Germany, etc. Research scientists in various countries were also approached. All new information was incorporated in the database (see Appendix 2 for the updated version). The database will continue to be revised throughout the duration of the project as and when new data becomes available.

Sample collection: 5-6/12/05
Sent to GBF: 12/12/05
Analysed by GBF: Jan 2006
Analysed by SOTON: Feb 2006

Publicly available data on Hg concentrations in effluents from wet FGD systems is very limited. More detailed information can be obtained only via personal contacts and by direct sampling. The mercury concentrations determined by SOTON and GBF in process water samples from U.K. power stations were lower than expected. Given the fact that wet FGD systems are known to remove significant quantities of reactive mercury from flue gases, it is surprising that Hg concentrations measured in scrubber liquids from coal-fired power stations appear to be in the microgram per litre range. This may be to do with the FGD system configuration, and is being investigated in more detail by studying process schemes and operating conditions. Mercury concentrations are also highly variable.

By contrast, in municipal waste incinerators Hg concentrations in scrubber liquids are consistently higher than in effluents from coal-fired power plants (milligram per litre range). However, these plants operate by a different principle and usually employ a highly acidic scrubber (pH<1). Similar conditions could be found at power stations only in plants operating with a pre-scrubber configuration. Efforts in year 3 will therefore concentrate on obtaining time-series samples from this type of plant.

Work carried out by GBF

A secrecy agreement was signed with SOTON and wastewater samples from coal fired power plant gas scrubbers obtained by SOTON and sent to the GBF were analysed. Mercury concentrations were in the ppb range and thus too low for microbiological treatment. It is unclear if these scrubbers effectively remove mercury, which is later perhaps precipitated as gypsum, and if the mercury concentrations in the gypsum are a problem.

On the other hand, some plants use acidic prescrubbers (pH < 1) which contain mercury in the ppm range. Treatability experiments with such scrubber wastewater from a municipal waste incinerator in Germany were successfully conducted by GBF and TU-BS.

List of deliverables for work package 4

Del. no.	Deliverable name	WP no.	Date due	Actual delivery date	Lead contractor
D13	Database of mercury emissions from coal fired power plants and municipal waste incinerators	4	Feb 05	Jun 05	3
D14	Assessment of control options for mercury	4	Feb 06	Mar 06	3
D15	Case study report on coal fired power plants etc.	4	Aug 06	Mar 07	3
D16	Final project meeting in England	8	Mar 07	Mar 07	3

Work package 5: Oil and Gas Industry

Objectives and starting point

Mercury in oil and gas has recently been recognized as one of the major technological and ecological threats, in particular in some tectonic structures and young folded belts of gas-oil and gas deposits where mercury is present at very high concentrations. Gas and oil exploitation can therefore represent a significant source of mercury as a by-product. The main objectives of these WP are:

1. to compile data on mercury concentrations in various areas of gas and oil exploitation and identify sources of major uncertainties for inventories of mercury emissions from these industrial sectors
2. to evaluate cleaning technologies for removal of mercury from gas and oil industry and identify in which phases (e.g. washing, major pre-treatments, etc.) biotechnology could play an important role
3. to investigate efficiency and safety of biotechnological cleaning methods based on data from previous experiments and feasibility studies conducted on samples from oil and gas industry
4. to identify uncertainties of data on mercury analysis and speciation in highly complex matrices (gaseous, liquid, solid) present in and originating from cleaning technologies in gas and oil industry
5. to assess the cost-effectiveness of different options for removal of mercury in oil and gas industry

Progress towards objectives

This work package proved extremely difficult. Dealing with industrial pollution of potential ecological and economic consequences caused a number of problems, including

- lack of published data
- questionable quality of published analytical data,
- lack of information on waste streams,
- difficulty of obtaining representative samples.

At the same time, combustion and processing of fossil fuels (coal, oil and gas) is an ongoing source of amospheric mercury pollution and the largest one on a global scale. Therefore, it would be necessary to approach the problem on an European scale.

All deliverables were provided.

Work carried out by JSI

Activity 1: During the mid-term meeting of the BIOMERCURY project it was concluded that the Deliverable No. 17, which summarizes the mercury related problems in oils and

gas industry will further be improved with new data. Therefore collection of data for the on mercury in gas and oil industry from various sources was continued. Unfortunately the new data originate from Canada in Thailand, while new data for Europe were still difficult to obtain. The new data are being incorporated in the updated version of Deliverable 17.

Activity 2. A report on mercury cleaning technologies and identification of possible technological options has been completed. The approach chosen is based on the whole cycle approach.

Activity 3: New set of samples were analyzed from the gas treatment facility in Molve, Croatia, and the report is being prepared to improve the needs for a report on Ina Naftaplin natural gas treatment facility in Molve. Due to the fact that the condensate, which is the most contaminated liquid sample is further used in the oil refinery in Sisak, Croatia, a decision was taken by the research group at IJS to also include refinery in Sisak in the whole cycle approach analysis.

Work carried out by SOTON

As was agreed at the mid-term assessment meeting in Braunschweig, SOTON also tried to assist with workpackage 5. The following data was collected on mercury emissions from the oil & gas industry in the U.K:

(a) Hg emissions from oil refineries in England and Wales, 1998-2004 (Source: U.K. Environment Agency Pollution Inventory)
(b) Hg emissions from the oil & gas sector in Scotland (Source: Scottish Pollutant Release Inventory, SPRI)
(c) Emissions reported to EPER for U.K. oil and gas refineries in 2001 (Source: European Pollutant Emission Register, EPER)

A number of direct written and telephone enquiries were also made:

(i) Esso Refinery at Fawley near Southampton: They have no mercury-containing wastewaters. Hg in discharge water is similar to the incoming salt water which they use for cooling purposes (~0.01-0.03 ug/l).
(ii) BP Grangemouth Refinery (emitted 10.6 kg of Hg to water in 2002 according to EPER): Hg concentrations in wastewater are only about 1.8 ppm (after biological treatment). Concentrations before treatment are not determined. Since they comply with the discharge limits, they see no need for any technology.
(iii) Shell Stanlow (emitted 25.9 kg of Hg to air in 2002 according to EPER, but only 5 kg according to U.K. Environment Agency data): It is company policy not to take part in any research, surveys, questionnaires etc., therefore the telephonist blocks all the calls and it is impossible to get through to anybody. They would not release the name of the Head of Environment and they made it clear that there is no point in phoning or writing letters.

Work carried out by GBF

The report by JSI about mercury in oil and gas industries was extensively discussed at the Midterm Assessment Meeting in Braunschweig. There is a huge need for more precise primary data on mercury in fossil fuels and the fluxes of mercury to the atmosphere.

In the context of the Biomercury project, there is also a need for data on mercury speciation during oil and gas processing, especially about the occurrence of ionic mercury in process water and gas scrubbers.

Condensate samples from the Naphta natural gas processing facility were sent by JSI to GBF and analysed for mercury concentrations by TU-BS. Low mercury concentrations were found, which consisted mainly of elemental mercury. This type of gas condensate is therefore not suitable for biological treatment.

The following preliminary conclusions can be drawn at this point:

1. Mercury in natural gas and in gas condensates occurs mainly in the elemental form. However, mercury containing wastewaters may be produced during washing of sour gas.
2. Mercury in oil occurs in many chemical forms, including Hg(0), Hg(II), and organomercury compounds. Total mercury concentrations in crude oil can be very high (up to 4 ppm). The fate of this mercury is largely unknown. There is no mass balance of mercury during processing of oil.
3. During processing of oil, many types of wastewater occur. The refinery processes and wastewater cleaning procedures are complex and different in the various factories. Ultimately, the wastewater enters a biological treatment plant. Any mercury which is entering the biological treatment plant is microbiologically converted to Hg^0 and released into the atmosphere.
4. There may be mercury contaminated wastewater produced during oil and gas processing which contain mercury in the mg/l (ppm) range, but very little data exist on mercury concentrations in these wastewaters.
5. One very important type of refinery wastewater is desalter water. The desalter is a big contributor of process wastewater. About 40 – 100 l are produced per ton of feedstock desalted. Mercury concentrations in the sludge/water are in the range of 0,01 to 41 ppm (mg/l). The reason for this huge range is unknown. This wastewater would in principle be suitable for microbiological cleaning. It contains other contaminants in addition to mercury, because process wastewater is often recycled for used in the desalter. More data would be needed.

List of deliverables in WP5

Del. no.	Deliverable name	WP No.	Date due	Actual delivery date	Lead contractor
D17	Summary report on mercury in oil and gas industries	5	Feb 05	May 05	7
D18	Report on cleaning technologies for removal of Hg from oil and gas	5	Feb 06	Jun 06	7
D20	Case study at Ina Naftaplin natural gas treatment facility	5	Feb 06	Feb 07	7

Work package 6: Novel Integrated Engineering Solutions

Objectives and starting point

This workpackage focuses on an overall engineering view of remediation processes of mercury polluted sites and mercury carrying waste streams. Such decontamination technologies commonly require the combined use of several physical, chemical and biological steps. The project specifically aims at the development of integrated concepts which essentially incorporate a biotechnological process stage. On the basis of the data delivered from the case studies and other sources, engineering methods will be applied for preliminary designs and cost calculations. The objective is to propose feasible and cost-effective solutions. From these analyses, follow-up projects will be developed in WP8.

Basis of any engineered conceptual process designs is the availability of appropriate data. This data covers site location, size of contamination, expected flows, treatment time, climatical relations, thermodynamic equilibria, rate of involved physical transport phenomena and kinetic information of the various process stages. The required data will be delivered from data banks and the various case studies in a cooperative approach. Additional information can be extracted from a number of reports (Eur. Commission, EPA, UNEP) and is available from our previous comprehensive work e.g. the development and long-time operation of the microbiological mercury removal process. - Dependent on the specific remediation case and the predominating boundary conditions alternate process routes will be designed and preliminary cost estimations carried out by using proven engineering methodologies. Criteria such as volume (place) and material demand, process reliability and robustness, ability for scale-up, flexibility to load alterations and costs will be applied to discriminate among rival routes.

Progress towards objectives

Information was distributed to all participants. In principle, integrated engineering solutions can only be developed during the end of the project. However, for the soil wash pilot plant at Vlora, Albania, an integrated optimised process scheme was developed.

Work carried out by TU-BS

All participants of the Biomercury project were given detailed information about our biological mercury remediation plant and they were informed about the principle of the microbial mercury resistant bacteria. In a presentation was shown that we are only able to clean ionic mercury and their must be the possibility to transfer mercury into the aqueous phase as Hg(II). We pointed out that for each case essential information are required like:

- Scope (mass, volume, concn., Hg speciation, flow rates etc.
- Accompanying Materials (salt loading, toxic compounds, effect on speciation and microbial consortia)

- Proven / Proposed Remediation Routes (conditions, performances, throughputs, effectiveness)
- Cost Estimates
- Environmental / Social Impacts

Analysis of available data, evaluation and proposal of feasible process route was done especially with participant 4 (GEOTEST) and 9 (AIPET). A detailed transfer of results and information was done with participant 1 (GBF) and participant 6 (TUL).

As deliverables (D26) a scheme was constructed for a process route in Workpackage 2.

In addition various samples deliverd from the WP 1, 2 and 4 were analysed.

On the Biomercury kick-off meeting the other participants were informed about our technology. At the International Conference on Mercury as a Global Pollutant in Ljubljana in June 2004 the public was informed about the technology within 2 talks

- Operation of a Mercury Removing Bioreactor at Chloralkali Factories in Europe
- Clean-up Strategies for Microbial Mercury Removal from Contaminated Environments

During the project meeting and workshop for chloralkali industry held in Lodz (Poland) in December 2004 the invited chloralkali members were informed with the talk "Longterm Operation of a Mercury Removing Bioreactor at Chloralkali Factories in Europe". In this presentation they got information about the principle function, the longterm performance and cost comparison of the BIOMER plant.

Work carried out by GEOTEST

The starting date of GEOTEST's activities on WP6 was March 2005.
The initial plans for WP6 included:

- Technological tests, analyses and tests for the improvement of the technology efficiency;
- Production and installation of a netting board to increase the efficiency of the technology;
- Implementation of new measures and a new long-term test operation (06–11/2005);
- Obtaining and evaluation of data from the new test operation;
- Evaluation of the test operation and design of improvements of the technological process;
- Sampling and research of the soil, the technological water and the sediments during long-term test operation;

During the reporting period the following activities within WP6 were performed:

1. Demonstration of the practical operation of the technology and explanation of principles of the technology used in Vlora within the workshop and the conference in Tirana.

2. Technological tests, tests and analyses for the improvement of the technology efficiency (microscopy, sedimentation tests, grain-size analyses)
3. Production and installation of a netting board to increase the efficiency of the technology. Performance of related changes in the electric wiring, in the connection of technological water and in the layout of other devices. Maintenance of the process equipment. Assembly of the imported device and installation, tests.
4. Excavation of contaminated soil (170 m^3) and test operation of the line. During operation, monitoring of input (24 samples) and output (32 samples) concentrations of mercury in soils, quality of technological water (6 samples) and concentration and forms of mercury in technological water, sediments from accumulation tank and clarifying tank (16 samples).
5. Trial operation of the line in the regime of repeated re-treatment of material.
6. Concentration of the obtained mixture of metallic mercury and soil.
7. Registration of the obtained product (metallic mercury) and its composition in double-jacketed packages (a total of 153.3 kg of metallic mercury obtained).
8. Documentation and collections of samples in the area of the excavation pit in the southern and southwestern zones in front of the electrolysis building. Overall, 10 soil samples taken.
9. Sampling of sediment from the accumulation tank and of technological water for the detremination of alkylated forms of Hg (analysed in Ljubljana, M. Horvath, Participant 7).
10. Laboratory works and analyses of soil, water and technological samples in connection with the preceding points.
11. Evaluation of the test operation.

List of deliverables for WP6

Del. no.	Deliverable name	WP No.	Date due	Actual delivery date	Lead contractor No.
D24	Process routes for different case studies	6	Aug 05	Feb 05	2
D25	Optimum reactor design for biotransformations	6	Feb 07	Feb 07	2
D26	Complete process design and cost evaluation	6	Feb 07	Feb 07	2

Work package 7: Biomercury Competence Center

Objectives and starting point

The BIOMERCURY competence center pursues the following objectives:

1. to develop a comprehensive database and website on worldwide mercury pollution and clean-up options based on the information gathered by all partners, in addition to the general project website;
2. to perform treatability studies in small scale on selected samples using microbiological methods;
3. to monitor the longterm performance of the first industrial bioreactor at SPOL Chemie, Czech Republic;
4. to define follow-up R&D projects, demonstrations or full-scale remediation work;
5. to seek appropriate funding for such projects.

Progress towards objectives

During the reporting period, the Biomercury website was regularly updated to include information accumulated during the project.

Treatability studies were supervised on samples from the industrially contaminated areas at Pavlodar (WP1) and Vlora (WP2), as well as on a waste air scrubber and mixed chemical wastewater (D28).

In addition, experiments for the use of coated electrodes for mercury determination were successfully conducted (HUJ).

Several grant applications were cooperated with. Two of them have been granted:

1. Humboldt-Fellowship for Prof. Jesus Olivero-Verbel, University of Cartagena, Columbia, to join the laboratory of Dr. Wagner-Döbler for one year.
2. Grant from the Polish Government for Prof. Ledakovicz, and Dr. Gluzcz, TUL, to operate a microbiological pilot plant at ZA Tarnow, Poland.

Work carried out by GBF

1. Biomercury website

The Biomercury website was designed by GBF and is in the Internet since February 2005 under the following URL:

www.biomercury.de

In May 2006 the number of accessions to the website was **11.220**.

2. Treatability studies

Microbiological treatability studies were designed and supervised for selected samples from
WP1 Industrial Area, Pavlodar, Kazakhstan (see report of TU-BS)
WP2 Hot Spot of Pollution, Vlora, Albania (see report of TU-BS)
WP3 Chloralkali electrolysis (see report of TUL)
WP4 Coal Fired Power Plants and Municipal Waste Incinerators (see report of TU-BS).

3. Follow-up studies

GBF supported GEOtest in an application for the EU program "Cards – strengthening of the environmental monitoring system. 2005/S 94-092528 Albania", Publication reference AuropeAid/121271/C/SV/AL.

GBF supported TUL to obtain funding for a research grant from the Polish government for microbiological clean-up of chloralkali electrolysis wastewater, including pilot operation at the electrolysis factory in Tarnow.

Work carried out by SOTON

The following awareness raising initiatives were carried out so far:

- A technology description and information on the BIOMERCURY website was sent to a senior policy analyst at the U.S. EPA who offered to 'spread the word' about this technology. Subsequently a lot of activity from the U.S. was registered on the BIOMERCURY website.
- Networking activity to include information on the BIOMERCURY technology in the EURODEMO (European Co-ordination Action for Demonstration of Efficient Soil and Groundwater Remediation) database (http://www.eurodemo.info/). EURODEMO aims to be the principal European co-ordination activity for soil and groundwater remediation technology demonstrations and is funded by the European Commission within the 6th Framework Programme.
- All coal-fired power stations in the U.K. were approached regarding the provision of scrubber liquid samples for treatability studies. They were also sent a questionnaire and asked whether they wanted to be kept informed about technology developments.
- A new Technology Platform on 'Zero Emission Fossil Fuel Power Plants'* was launched by the Commission in December 2005. The main objective of this initiative is to drastically reduce the environmental impact of fossil fuels, and particularly coal. The Platform includes important stakeholders from industry, government, and research institutions, who will define strategic research goals for the medium to long term and establish the necessary public-private partnerships for their implementation. A letter was written to Denis O'Brien, the Commissioner primarily associated with the new platform, to highlight the importance of reducing Hg emissions as well as CO_2 emissions. The suggestion was made to tackle the Hg issue by setting up an additional working group under the general umbrella of the platform.
  *(**http://europa.eu.int/comm/research/energy/nn/nn_rt/nn_rt_co/article_2268_en.htm**)

Efforts to increase awareness on the importance of Hg emissions monitoring in the power industry on both national and European levels will continue in Period 3.

Work carried out by HUJI

We have started working on the development of a simple electrode for the detection of low levels of mercury in aqueous solutions by voltammetry. The electrode is currently based on spin-coating a 7x15 mm indium-tinoxide (ITO) surface by a sol-gel thin film, in which a selective host-molecule for Hg^{II} is incorporated. We are using the macrocyclic molecule Kryptofix 222. We have developed a method for the formation of very thin films that are approximately 20-50 nm, which we hope will be ideal for electroanalytical purposes. A manuscript, describing the approaches used for preparing such thin films will be submitted soon for publication.
Following is the abstract of this paper:
The formation and characterization of nanometer thick sol-gel films is reported. The films were prepared by spin-coating of a diluted solution of silane precursor on a number of different substrates. The effect of dilution, rotation speed and nature of substrate on the thickness and homogeneity of the films was examined. Characterization of the films was carried out by profilometry, reflectance spectroscopy, atomic force microscopy, adhesion test and electrochemistry. We find that the dilution factor has a pronounced effect on the film thickness. Moreover, the time of dilution, namely, whether dilution was carried out before or after a period of hydrolysis, had a noticeable effect on the permeability of embedded species.

List of deliverables for WP7

Del. no.	Deliverable name	WP No.	Date due	Actual delivery date	Lead contractor
D2	Feasibility study	1	Feb 06	Feb 05	1
D6	Report on treatability	2	Feb 06	Feb 05	1
D27	Biomercury database and website	7	Feb 07	Feb 05	1
D28	Comprehensive reports on treatability studies	7	Feb 07	Feb 07	1
D38	Project website	8	May 04	Feb 05	1

Work package 8: Workshops and Conferences

General background

The international composition of the Biomercury consortium makes it impossible for contractors to attend all meetings, because these costs would be much higher than the allowed budget. Therefore, general project meetings are coupled to case study related meetings (e.g. meeting for Chloralkali industries, meeting in Tirana about Vlora Hot Spot of Pollution) or to International meetings (7th ICMGP in Ljubljana). Contractors have to decide individually (based on the status of their work package, the place and topic of the meeting) if participation in a particular meeting is desirable and justifiable.

Work carried out by GBF

The GBF organized the **midterm assessment meeting** in **Braunschweig, Germany**, from **14.-15. September 2005.**
After the meeting, a field trip was organised to the underground storage site for highly hazardous waste, which is unique within Europe. It is operated by K&S Entsorgung GmbH and located in Eastern Germany.

Changes to work plan

The following meeting was cancelled because of too high costs:

Workshop on Pavlodar Former Industrial Area
Almaty, Kazakhstan, April 2006; Organizer: AIPET

Instead, the second year project meeting was from **18.-19.5.2006** in **Prague, Czech Republic**, and was organized by **Geotest**.

Work carried out by UT-LACH

Organisation of the following meetings:

- "**Workshop on Vlora Hot Spot of Pollution", Tirana, Albania, 26.-27.4.2005**
- Field trip to the abandoned industrial area in Vlora, Albania.
- Biomercury project meeting, Tirana, Albania, 26.4.2005

Work carried out by TUL

Organisation of the **Workshop for Chloralkali Companies, December 2004**

Work carried out by JSI

Organisation of a bioremediation session at the **7th Conference on Mercury as a global Pollutant, June 2004, Ljubljana**, Slovenia.

Work carried out by SOTON

Organization of **the final project meeting at the University of Southampton,** England.

Work carried out by Geotest

Participation in the workshop on Vlora Hot Spot on Pollution – Bioremediation of Mercury from the Contaminated Areas (26 – 27 April 2005) – oral and poster presentation in Tirana, Albania (one contributed paper under the titĺe "Revitalization of the Land Contaminated with Mercury in the Area of the Former Production of Cl-PVC in Vlora, Albania" and 4 posters; demonstration of operation of pilot technology in Vlora).

Participation at the midterm assessment meeting in Braunschweig, Germany 13 – 16 September 2006. Presentation of the process of the pilot operation of the removal of mercury from soil at the Vlora site. Explanation of the improvements done on the decontamination line.

Organization of the second year project meeting from **18.-19.5.2006** in **Prague, Czech Republic.**

List of deliverables for WP8

Del. no.	Deliverable name	Date due	Actual delivery date	Lead contractor
D30	Biomercury session at 7th ICMGP, Ljubljana, June 2004	June 05	June 05	7
D33-1	Kickoff meeting of Biomercury project at ICMGP	June 05	June 05	1
D12	Workshop for chloralkali industries	Feb 05	Dec 04	6
D33-2	Project meeting, Lodz, Poland	Dec 04	Dec 04	1
D8	Symposium in Albania	Apr 05	Apr 05	8
D33-3	Project meeting, Tirana, Albania	Apr 05	Apr 05	1
D33-4	Midterm assessment meeting, Braunschweig, Germany	Sep 06	Sep 06	1
D4	Meeting in Prague, Czech Republic	Mar 06	May 06	4
D33-5	Project meeting, Prague, Czech Republic	Mar 06	May 06	1
D16	Workshop in England	Mar 07	Mar 07	3
D33-6	Project meeting 2007, England	Mar 07	Mar 07	1

Work package 9: Project Management

The project management was done by the coordinator (**GBF**). GBF supervised all work packages and supported the partners with logistic help.

During the second project year, an intermediate management report was compiled by GBF. GBF also produced the midterm assessment report for the European commission.

The project management assisted with the organisation of project meetings and prepares meeting protocols. It handled the communication with the European Commission, all financial matters and project controlling.

The project management regularly updated the Biomercury website (D38).

List of deliverables for WP 9

Del. no.	Deliverable name	WP No.	Date due	Actual delivery date	Lead contractor
D35	Preparation of project meetings	9	Jul 04 Dec 04 Apr 05 Sept 05 May 06 Mar 07	Jul 04 Dec 04 Apr 05 Sept 05 May 06 Mar 07	1
D36	Protocols of project meetings	9	Jul 04 Dec 04 Apr 05 Sept 05 May 06 Mar 07	Jul 04 Dec 04 Apr 05 Sept 05 May 06 Mar 07	1
D37	Reports to European Commission	9	Apr 05 Jul 05 Sep 05 May 06 Apr 07	Apr 05 Jul 05 Sep 05 May 06 Apr 07	1
D38	Project website	9	May 04	Feb 05	1

Section 4 Other Issues

Additional Case study reports on mercury polluted areas

D39 Industrial Area North Coast of Colombia and Chloralkali Plant, Cartagena, Columbia

D 40 Land use change and Hg remobilisation in the Amazon

The scientific reports on these case studies were conducted by UC (contr. 10) and LABOMAR (contr. 11). They are presented as additional deliverables (D39 and D40).

Microbial Mercury Remediation as Best Available Technology

D41 Microbial Mercury Remediation as Best Available Technology

Period 3 Management Report

Section 1 Justification of major cost items and resources

Brief description of the work performed

Work package 1 – Industrial Area, Pavlodar, Kazakhstan

GBF (contr. 1)

- advice on methyl mercury sampling
- supervision of treatability study with Pavlodar samples
- selection, cultivation and identification of microorganisms for treatability study

TU-BS (contr. 2)

- Solid samples from Kazakhstan were sent to TUBS for Hg analysis
- Bioremediation studies with artificial contaminated soil were done at the TUBS Exchange of information

SOTON (contr. 3)

- organise the collection and transport of two groundwater samples and one large sediment sample from the Pavlodar industrial site
- ship groundwater samples to partner 7 (IJS) for speciation analysis
- ship sediment sample to GBF for analysis and use in bioremediation experiments

JSI (contr. 7)

- analysis of samples

AIPET (contr. 9)

- An article (in Russian language) on history and current condition of mercury contamination in Pavlodar (60 pages) was prepared and placed on web-site http://Hg-Pavlodar.narod.ru;
- Three years project 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» has started of January 2006;
- Sampling of both ground water from observation boreholes and bottom sediment from wastewater storage pond - Lake Balkyldak were carried out.

UC (contr. 10)
Industrial Area. North Coast of Colombia.

Air mercury data have been collected around the industrial zone of Cartagena City as well as in different rooms at the Pharmaceutical building of the University of Cartagena. A paper has been submitted to B*ulletin of Environmental Contamination and Toxicology* (MedLine indexed Journal).

LABOMAR (contr. 11)
Madeira River Basin, Amazon

- Short course on Biogeochemistry of Trace Metals, with emphasis on Hg at the 28^{o} annual meeting of the Brazilian Chemical Society, Pocos de Caldas, Brazil, 30 may-02 June, 2005.
- Oral and panel presentations on the project results at the XIII International Conference on Heavy Metals in the Environment, Rio de Janeiro, Brazil, 7-10 June 2005.
- Review of the published literature
- Contacts with research personnel at the University of Rondônia to prepare field campaigns on the Hg presence in tropical rain forest and litterfall studies

Work package 2 - Hot Spot of Pollution, Vlora, Albania

GBF (contr. 1)

- discussion of Vlora data at project meetings
- presentation of microbial technology at Vlora meeting in April 2005
- supervision of treatability study with Vlora sample

TU-BS (contr. 2)

- Meeting in Albania (25 – 28. April 05)
- Explanation of the Operation of the Soil Wash Plant from GEOTEST
- Completion of the mercury mass balance
- Taking samples for Hg measurement and further remediation of the sludge from the sedimentation basin

JSI (contr. 7)

- analysis of samples

UT-LACH (contr. 8)

- Organization of the workshop on Vlora Hot Spot Pollution, Tirana (meeting in Tirana and trip in Vlora ex-Chlor Alkali Plant)
- oral presentation on actual mercury pollution at the Vlora ex-Chlor Alkali Plant site at the workshop on Vlora Hot Spot Pollution, Tirana
- Posters presentation (4 posters) at the workshop on Vlora Hot Spot Pollution, Tirana
- discussion of new situation of Vlora ex-Chlor Alkali Plant after the intervation from some companies having business activity on the area (midterm assesment meeting of the group)
- preparation of new data on contamination of Vlora ex-Chlor Alkali Plant using for database of mercury pollution at Vlora ex-Chlor Alkali Plant site (deliverable D5))
- gathered information on the history of Vlora ex-Chlor Alkali Plant, its operating technology, source of pollution during the operation period and after closed of the plant for inclusion in the report of Vlora site, aiming to complete assessment of pollution problem of this site (D7)
- review of the published literature

- oral presentation on actual situation on mercury pollution at Vlora ex-Chlor Alkali Plant site reported in Midterm Assessment Meeting, Biomercury, 14. – 15.9.2005, GBF, Braunschweig, Germany
- Poster presentation reported in Midterm Assessment Meeting, Biomercury, 14. – 15.9.2005, GBF, Braunschweig, Germany
- Updating the results of Hg content in soils before and after cleaning process (analysis of 12 soil samples)
- Updating the results of Hg content in hair samples of the children living inside territory of Vlora Hot Spot pollution (analysis of 22 hair samples), aiming to complete the data on mercury pollution of the Adriatic Sea as well as mercury concentrations in hair of people living on this site, the data which will be included in the final case study report
- Optimization of the analytical methods for the determination of Hg_{tot} in urine samples and Hg_{tot}, MeHg in fish and mussel samples.
- Preparing the intermediate report of Vlora Hot Spot pollution (50 pages)

Work package 3 - Chloralkali Electrolysis Industry

GBF (contr. 1)

- Presentation of the microbiological clean-up technology at the meeting with the director of the electrolysis factory at Tarnow, Poland, April 2006
- Consulting on pilot operation of microbial technology at Tarnow
- Supervision of treatability studies with electrolysis wastewater
- Supervisison of Phd student, Katarzyna Zakrzevska

TU-BS (contr. 2)

- Provide instructions for microbiological experiments to the TUL so that they can do treatibility studies with activated carbon and the mercury resistant microbes
- Provide mercury resistant microbes to the TUL
- Supervision of member of TUL at the TUBS for operation of bioreactors with activated carbon as support material
- Meeting with a German chlor alkali factory. Provide information about the investment and operation costs for a full scale biological mercury removal plant. Calculation / pre construction of full scale pre-treatment unit.
- Treatibility study of wastewater from a German chlor alkali factory

TUL (contr. 6)

- bioreactor experiments with activated carbon
- bioreactor experiments with mercury resistant bacteria
- establishing contacts with EIPPC Bureau (Sevilla, Spain), Polish Chamber of Chemical Industry and “Responsible Care” Program, in order to gain the information about usual way of recommendation of a new wastewater treatment technology to the IPPC Reference Document and to the local industry.

AIPET (contr. 9)

- An article in Russian language about mercury pollution in Live have been prepared and placed on web-site http://Hg-Kiev.narod.ru;

UC (contr. 10)

- A collaborative paper with the Microbiology Department of the University of Cartagena has been completed and submitted to *Biomedica* (MedLine indexed Journal). This paper deals with mercury- and antibiotic-resistance bacteria found in Cartagena Bay, a waterbody polluted by effluents from a Chloralcali industry.

Work package 4 - Coal Fired Power Plants and Municipal Waste Incinerators

GBF (contr. 1)

- supervision of scrubber sludge sample analysis
- treatability study with scrubber sludge sample from pilot waste incinerator TAMARA
- selection, cultivation and identification of microorganisms for treatability study

TU-BS (contr. 2)

Hg contaminated water samples from different scrubber facilities were sent to TUBS from SOTON for mercury analysis.

SOTON (contr. 3)

- continue to gather information on mercury emissions and releases from coal-fired power plants and municipal waste incinerators for database (D13)
- find out location and addresses of all U.K. power stations and send out questionnaire in order to gather additional data for database (D13)
- finalise database on mercury emissions and releases from coal-fired power plants and municipal waste incinerators (D13) and forward to co-ordinator
- approach all coal-fired power stations in the U.K. regarding the provision of samples for treatability studies
- follow-up written and telephone enquiries
- negotiate with power stations, conclude confidentiality agreement, collect samples
- ship power station samples to GBF for analysis of total mercury content in the liquid phase
- determination of mercury concentrations in remaining power station samples at SOTON (liquid and solid phase)
- collect information on control options
- write work package report on assessment of control options for mercury (D14)

AIPET (contr. 9)

- Assessment of available information relating to mercury emissions and releases as a result of operation of power plants and municipal waste incinerators in Kazakhstan (D13).

Work package 5 - Oil and Gas Industry

GBF (contr. 1)

- discussion of data and possible treatability study at project meetings
- supervision of sample analysis from Naphta gas plant

TU-BS (contr. 2)

- Condensate samples from Croatian gas industry were sent by JSI to the TUBS for investigation
- Condensate samples were measured for total and metallic mercury. Different tests for extraction of mercury from the condensate in the water phase were done. Discussion with JSI about different analysis problems and the technical relevance for the gas industry to oxidise condensate samples.

SOTON (contr. 3)
- collate data on mercury emissions from the oil & gas sector in Scotland, England and Wales from various pollution inventories
- make written and telephone enquiries to oil refineries in the U.K.
- search for and forward additional measurement data on Hg concentrations in oil and gas samples and various research articles and other documents

JSI (contr. 7)
- analysis of sample
- reporting
- cost-benefit analysis

Work package 6 - Novel Integrated Engineering Solutions

GBF (contr. 1)
- Design of treatability studies in cooperation with TU-BS

TU-BS (contr. 2)
- evaluation of process scheme
- mass balance
- optimization of process routes
- design of novel microbiological approaches

GEOTEST (contr. 4)
- Technological tests, analyses and tests for the improvement of the technology efficiency;
- Production and installation of a netting board to increase the efficiency of the technology;
- Implementation of new measures and a new long-term test operation (06–11/2005);
- Obtaining and evaluation of data from the new test operation;
- Evaluation of the test operation and design of improvements of the technological process;
- Sampling and research of the soil, the technological water and the sediments during long-term test operation;

UC (contr. 10)
Gold and Mercury Mining.

- Data collection on mercury in hair have been gathered for several communities living along the Cauca and the Magdalena Rivers, located at different distances downstream the gold mining area. Samples have been taken from the communities of San

Martín de Loba, Altos del Rosario, Hatillo de Loba, Magangue, Soplaviento and La Raya, north of Colombia.

- Mercury levels in fish have been measured in several stations along the Diquel Channel (Gambote, Soplaviento and Maria La Baja), the most distant places from the gold mining area, with marshes where polluted sediments are deposited.

- These data have been transferred into a geographical information system (GIS) to generate maps on human mercury pollution in these areas. This map will be distributed in all communities and will be uploaded in internet.

Work package 7 - Biomercury Competence Center

GBF (contr. 1)
- maintenance and update of biomercury website
- compilation of material for website
- providing information to project partners
- supervision of treatability study

TU-BS (contr. 2)
- new experimental concepts
- exchange of information

SOTON (contr. 3)
- approach contact at the U.S. EPA to spread information on the BIOMERCURY technology in the U.S. and worldwide
- networking activity to include information on BIOMERCURY bioremediation process in the EURODEMO database
- approach all coal-fired power stations in the U.K. regarding the provision of samples for treatability studies & questionnaire
- approach new Technology Platform on 'Zero Emission Fossil Fuel Power Plants'

HUJI (contr. 5)
- new experimental concept for mercury measurement

LABOMAR (contr. 11)
- Provision of reference materials, reprints and pre-prints for Biomercury project database and website

Work package 8 - Workshops and Conferences

GBF (contr. 1)
- several presentations, poster at Tirana meeting
- Organization of midterm assessment meeting in Braunschweig, several presentations and poster
- Special meeting with chloralkali electrolysis company, Tarnow, Poland

TU-BS (contr. 2)
- 1-day business trip to a German chlor alkali factory (19.5.05)

- participation in Tirana meeting
-

SOTON (contr. 3)

- prepare poster on 'Mercury emissions from coal-fired power plants and waste incinerators'
- participate in mid-term review meeting in Braunschweig, 14-15 September 2005

GEOTEST (contr. 4)

- sampling trips to Vlora

TUL (contr. 6)

- participation and oral presentation at the 12th Congress on Biotechnology, Copenhagen, Denmark – August 2005;

paper presented by P. Głuszcz: "Modification of the microbiological method for mercury remediation from industrial wastewater";

- participation and oral presentation at the Biomercury project Intermediate Assesment Meeting in Braunschweig, Germany – September 2006 (S. Ledakowicz, P. Głuszcz , K. Zakrzewska);
- visit at the Chemical Company "Rokita" S.A., Brzeg, Poland, in order to get chlor-alkali wastewater samples and to discuss economical and technical aspects of wastewater treatment in the factory;

JSI (contr. 7)

- preparation of the proposal
- participation of Drs. Milena Horvat and Andrej Stergaršek at the midd-term meeting in Germany.
- Sampling at Ina naftla plin Molve, croatia

UT-LACH (contr. 8)

- Participation in the workshop on Vlora Hot Spot Pollution, Tirana (meeting in Tirana and trip in Vlora ex-Chlor Alkali Plant) and midterm meeting in Tirana (26, 27 Appril, 2005) (D8, D30)
- Participation in Midterm Assessment Meeting, Biomercury, 14. – 15.9.2005, GBF, Braunschweig, Germany

AIPET (contr. 9)

- ISTC workshop, Moscow
- Sampling trips to Pavlodar Chemical Plant

UC (contr. 10)

- The Colombian partner of the project attended the Midterm Assessment meeting that took place from 14. – 15. September 2005, at the National Research Center for Biotechnology (GBF) in Braunschweig, Germany. The purpose of this travel was to present the results obtained during the project in the participating Workpackages. (Colombian Pesos $3,470,836).
- Environmental sampling to different gold mining areas of the South of Bolivar to collect sediments, fish and human hair samples. (Colombian Pesos $5,000,000).

LABOMAR (contr. 11)

- 28º annual meeting of the Brazilian Chemical Society, Pocos de Caldas, Brazil, 30 may-02 June, 2005.
- XIII International Conference on Heavy Metals in the Environment, Rio de Janeiro, Brazil, 7-10 June 2005.
- Measurement trips

Work package 9 - Project Management

Work carried out by GBF:

- Compilation of reports to the European Commission
- Provides logistic help and information to all partners
- Supervision of treatability studies by TU-BS and GBF
- Financial guidance
- Juristic guidance
- Organisation of project meetings
- preparation of meeting protocols
- Updating the Biomercury website
- communication with the European Commission
- project controlling

Explanatory note on major cost items

Major purchases of investment or consumables were not undertaken.

Large consumable items

There were no large consumable items purchased in period 3.

Budgeted and actual costs

Budgeted and actual costs and person months for Period 3 are given in the Table 1 a-c below.

Deviations from cost budget and/or person-month budget

No major deviations from the budget occurred.

Table 1a

Cost Budget Follow-up Table

Contract N°:NMP2-CT-2004-505561-1 **Acronym: BIOMERCURY** **Date: 01.03.2005-28.02.2006**

PARTICIPANT	TYPE of EXPENDITURE (as defined by participants)	Total Budet 36 months	BUDGET Period 1 12 months	BUDGET Period 2 12 months	ACTUAL COSTS (EUR)				Pct. spent				Remaining Budget (EUR)
					Period 1	Period 2	Period 3	Total	Year 1	Year 2	Year 3	Total	
Part. 1 GBF	**Total Person-month**	**17**	**5,67**	**5,67**	13,64	20,82		**34,46**	241%	367%		203%	
	Personnel costs	**65.313,00**	**21.771,00**	**21.771,00**	27.066,87	36.177,83		**63.244,70**	124%	166%		97%	**2.068,30**
	Major cost item travel	**9.000,00**	**3.000,00**	**3.000,00**	5.280,01	32,77		**5.312,78**	176%	1%		59%	**3.687,22**
	Major cost item consumables	**1.000,00**	**333,33**	**333,33**	429,03	1.528,67		**1.957,70**	129%	459%		196%	**-957,70**
	Other costs, here: Consortium Management Activities	**26.091,00**	**8.697,00**	**8.697,00**	63,79	4.853,45		**4.917,24**	1%	56%		19%	**21.173,76**
	Total Costs	**101.404,00**	**33.801,33**	**33.801,33**	**32.839,70**	**42.592,72**		**75.432,42**	**97%**	**126%**		**74%**	**25.971,58**
Part. 2 TUBS	**Total Person-month**	**13,00**	**4,33**	**4,33**	4,33	5,50		**9,83**	100%	127%		76%	
	Personnel costs	**53.075,00**	**17.691,67**	**17.691,67**	5.957,05	28.906,88		**34.863,93**	34%	163%		66%	**18.211,07**
	Major cost item travel	**5.000,00**	**1.666,67**	**1.666,67**	210,10	839,45		**1.049,55**	13%	50%		21%	**3.950,45**
	Major cost item consumables	**0,00**	**0,00**	**0,00**	0,00	0,00		**0,00**	0%	0%		0%	**0,00**
	Total Costs	**58.075,00**	**19.358,33**	**19.358,33**	**6.167,15**	**29.746,33**		**35.913,48**	**62%**	**154%**		**62%**	**22.161,52**
Part. 3 SOTON	**Total Person-month**	**10,00**	**3,33**	**3,33**	3,60	4,00		**7,60**	108%	120%		76%	
	Personnel costs	**45.487,00**	**15.162,33**	**15.162,33**	18.608,00	21.512,00		**40.120,00**	**123%**	142%		88%	**5.367,00**
	Major cost item travel	**9.040,00**	**3.013,33**	**3.013,33**	2.000,00	1.706,00		**3.706,00**	**66%**	57%		41%	**5.334,00**
	Major cost item consumables	**2.640,00**	**880,00**	**880,00**	500,00	957,00		**1.457,00**	**57%**	109%		55%	**1.183,00**
	Total Costs	**57.167,00**	**19.055,67**	**19.055,67**	**21.108,00**	**24.175,00**		**45.283,00**	**111%**	**127%**		**79%**	**11.884,00**
Part. 4 Geotest	**Total Person-month**	**14,00**	**4,67**	**4,67**	9,47	15,87		**25,34**	203%	340%		181%	
	Personnel costs	**18.900,00**	**6.300,00**	**6.300,00**	7.526,84	17.987,20		**25.514,04**	119%	286%		135%	**-6.614,04**
	Major cost item travel	**9.000,00**	**3.000,00**	**3.000,00**	2.002,06	7.387,90		**9.389,96**	67%	246%		104%	**-389,96**
	Major cost item consumables	**2.500,00**	**833,33**	**833,33**	1.261,60	12.082,67		**13.344,27**	151%	1450%		534%	**-10.844,27**
	Total Costs	**30.400,00**	**10.133,33**	**10.133,33**	**10.790,50**	**37.457,77**		**48.248,27**	**106%**	**370%**		**159%**	**-17.848,27**
Part. 5 HUJI	**Total Person-month**	**6,00**	**2,00**	**2,00**	0,00	0,00		**0,00**	0%	0%		0%	
	Personnel costs	**12.063,00**	**4.021,00**	**4.021,00**	0,00	0,00		**0,00**	0%	0%		0%	**12.063,00**
	Major cost item travel	**3.150,00**	**1.050,00**	**1.050,00**	810,00	1.936,64		**2.746,64**	77%	184%		87%	**403,36**
	Major cost item consumables	**0,00**	**0,00**	**0,00**	0,00	0,00		**0,00**	0%	0%		0%	**0,00**
	Total Costs	**15.213,00**	**5.071,00**	**5.071,00**	**810,00**	**1.936,64**		**2.746,64**	**16%**	**38%**		**18%**	**12.466,36**

Table 1b

Cost Budget Follow-up Table

Contract N°:	NMP2-CT-2004-505561-1			Acronym: BIOMERCURY				Date:	01.03.2005-28.02.2006				
PARTI-CIPANTS	TYPE of EXPENDITURE (as defined by participants)	Total BUDGET 36 months	BUDGET Period 1	BUDGET Period 2	ACTUAL COSTS (EUR)				Pct. spent				Remaining Budget (EUR)
					Period 1	Period 2	Period 3	Total	Period 1	Period 2	Period 3	Total	
Part. 6 TUL	**Total Person-month**	**13,00**	**4,33**	**4,33**	6,00	7,50		**13,50**	138%	173%		104%	
	Personnel costs	**9.400,00**	**3.133,33**	**3.133,33**	0,00	3.850,24		**3.850,24**	0%	123%		41%	**5.549,76**
	Major cost item travel	**9.000,00**	**3.000,00**	**3.000,00**	2.035,45	4.011,00		**6.046,45**	68%	134%		67%	**2.953,55**
	Major cost item consumables	**7.500,00**	**2.500,00**	**2.500,00**	142,66	3.361,07		**3.503,73**	6%	134%		47%	**3.996,27**
	Total Costs	**25.900,00**	**8.633,33**	**8.633,33**	**2.178,11**	**11.222,31**		**13.400,42**	**25%**	**155%**		**52%**	**12.499,58**
Part. 7 JSI	**Total Person-month**	**8,00**	**2,67**	**2,67**	0,00	4,40		**4,40**	0%	165%		55%	
	Personnel costs	**21.000,00**	**7.000,00**	**7.000,00**	0,00	12.978,53		**12.978,53**	65%	185%		62%	**8.021,47**
	Major cost item travel	**9.000,00**	**3.000,00**	**3.000,00**	1.961,00	2.993,84		**4.954,84**	65%	100%		55%	**4.045,16**
	Major cost item consumables	**4.500,00**	**1.500,00**	**1.500,00**	0,00	1.412,10		**1.412,10**	0%	94%		31%	**7.587,90**
	Total Costs	**34.500,00**	**11.500,00**	**11.500,00**	**1.961,00**	**17.384,47**		**19.345,47**	**17%**	**151%**		**56%**	**15.154,53**
Part. 8 UT-LACH	**Total Person-month**	**19,00**	**6,33**	**6,33**	8,00	11,00		**19,00**	126%	174%			
	Personnel costs	**9.400,00**	**3.133,33**	**3.133,33**	3.000,00	3.400,00		**6.400,00**	96%	109%		68%	**3.000,00**
	Major cost item travel	**4.500,00**	**1.500,00**	**1.500,00**	2.100,50	1.383,56		**3.484,06**	140%	92%		77%	**1.015,94**
	Major cost item consumables	**1.000,00**	**333,33**	**333,33**	885,90	274,40		**1.160,30**	266%	82%		116%	**-160,30**
	Total Costs	**14.900,00**	**4.966,67**	**4.966,67**	**5.986,40**	**5.057,96**		**11.044,36**	**121%**	**102%**		**74%**	**3.855,64**
Part. 9 AIPET	**Total Person-month**	**24,00**	**8,00**	**8,00**	8,00	2,80		**10,80**	100%	35%		45%	
	Personnel costs	**11.592,00**	**3.864,00**	**3.864,00**	3.954,30	0,00		**3.954,30**	102%	0%		34%	**7.637,70**
	Major cost item travel	**7.500,00**	**2.500,00**	**2.500,00**	3.728,03	2.461,89		**6.189,92**	149%	98%		83%	**1.310,08**
	Major cost item consumables	**3.450,00**	**1.150,00**	**1.150,00**	18,47	69,90		**88,37**	2%	6%		3%	**3.361,63**
	Total Costs	**22.542,00**	**7.514,00**	**7.514,00**	**7.700,80**	**2.531,79**		**10.232,59**	**102%**	**34%**		**45%**	**12.309,41**
Part. 10 UC	**Total Person-month**	**6,00**	**2,00**	**2,00**	2,00	4,00		**6,00**	100%	200%		100%	
	Personnel costs	**4.550,00**	**1.516,67**	**1.516,67**	1.638,40	1.998,80		**3.637,20**	108%	132%		80%	**912,80**
	Major cost item travel	**7.400,00**	**2.466,67**	**2.466,67**	1.310,70	2.775,70		**4.086,40**	53%	113%		55%	**3.313,60**
	Major cost item consumables	**3.000,00**	**1.000,00**	**1.000,00**	0,00	1.187,50		**1.187,50**	0%	119%		40%	**1.812,50**
	Total Costs	**14.950,00**	**4.983,33**	**4.983,33**	**2.949,10**	**5.962,00**		**8.911,10**	**59%**	**120%**		**60%**	**6.038,90**

Table 1c

Cost Budget Follow-up Table

Contract N°:	NMP2-CT-2004-505561-1			Acronym: BIOMERCURY				Date:	01.03.2005-28.02.2006				
PARTI-CIPANTS	TYPE of EXPENDITURE (as defined by participants)	Total BUDGET 36 months	BUDGET Year 1	BUDGET Year 2	ACTUAL COSTS (EUR)				Pct. spent				Remaining Budget (EUR)
					Year 1	Year 2	Year 3	Total	Year 1	Year 2	Year 3	Total	
Part. 11 LABOMAR	**Total Person-month**	**6,00**	**2,00**	**2,00**	2,00	3,60		**5,60**	100%	180%		93%	
	Personnel costs	**4.550,00**	**1.516,67**	**1.516,67**	0,00	0,00		**0,00**	0%	0%		0%	**4.550,00**
	Major cost item travel	**7.400,00**	**2.466,67**	**2.466,67**	2.515,36	2.969,58		**5.484,94**	102%	120%		74%	**1.915,06**
	Major cost item consumables	**3.000,00**	**1.000,00**	**1.000,00**	546,72	0,00		**546,72**	55%	0%		18%	**2.453,28**
	Total Costs	**14.950,00**	**4.983,33**	**4.983,33**	**3.062,08**	**2.969,58**		**6.031,66**	**61%**	**60%**		**40%**	**8.918,34**
Part. 12 RUTGERS	**Total Person-month**	**0,67**	**0,67**	**0,67**				**0,00**	0%	0%		0%	
	Personnel costs	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Major cost item travel	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Major cost item consumables	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Total Costs	**0,00**	**0,00**	**0,00**	**0,00**	**0**	**0**	**0,00**	**0%**	**0%**		**0%**	**0,00**
Part. 13 USEPA	**Total Person-month**	**0,67**	**0,67**	**0,67**				**0,00**	0%	0%		0%	
	Personnel costs	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Major cost item travel	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Major cost item consumables	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Total Costs	**0,00**	**0,00**	**0,00**	**0,00**	**0**	**0**	**0,00**	**0%**	**0%**		**0%**	**0,00**
Part. 14 UFL-COE	**Total Person-month**	**0,67**	**0,67**	**0,67**				**0,00**	0%	0%		0%	
	Personnel costs	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Major cost item travel	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Major cost item consumables	**0,00**	**0,00**	**0,00**				**0,00**	0%	0%		0%	**0,00**
	Total Costs	**0,00**	**0,00**	**0,00**	**0,00**	**0**	**0**	**0,00**	**0%**	**0%**		**0%**	**0,00**
TOTAL	**Total Person-month**	**142,00**	**47,33**	**47,33**	26,44	79,49		**105,93**	74%	168%		75%	
	Personnel costs	**253.042,00**	**85.110,00**	**85.110,00**	63.046,71	126.811,48		**189.858,19**	74%	149%		75%	**63.183,81**
	Major cost item travel	**79.990,00**	**26.663,33**	**26.663,33**	30.346,72	28.498,33		**58.845,05**	114%	107%		74%	**21.144,95**
	Major cost item consumables	**28.590,00**	**9.530,00**	**9.530,00**	2.832,33	20.873,31		**23.705,64**	30%	219%		83%	**4.884,36**
	Other costs ('the rest'), here: Consortium Management Activities	**26.091,00**	**8.697,00**	**8.697,00**	6.050,22	4.853,45		**10.903,67**	70%	56%		42%	**15.187,33**
	Total Costs	**387.713,00**	**130.000,33**	**130.000,33**	**102.275,98**	**181.036,57**		**283.312,55**	**79%**	**139%**		**73%**	**104.400,45**

Section 2 Consortium Management

Deliverables List

Below is the complete list of deliverables in the Biomercury project. Deliverables shown in red were due at the end of the third project year and have been submitted with this report. A complete file of all deliverables is provided on the accompanying CD.

Del. no.	Deliverable name	WP no.	Lead partici-pant	Estimated person-months	Nature	Dissemina-tion level	Due date (month)	Status (%)	Delivered (month)
D1	Database on mercury pollution at the Pavlodar site	1	9	15.0	O	PU	12	100	12
D2	Feasibility study of selected samples by biological method	1	9	9.0	R	RE	24	100	12
D3	**Case study report on Pavlodar site**	**1**	**9**	**1.6**	**R**	**PU**	**30**	**100**	**34**
D4	**Symposium in Kazakhstan (changed to Prague)**	**1**	**9/4**	**1.5**	**O**	**PU**	**25**	**100**	**27**
D5	Report on Vlora pollution	2	8	14.0	R	PU	12	100	12
D6	Report on treatability study with microbiological method	2	8	6.0	R	RE	24	100	12
D7	**Case study report on Vlora hot spot of pollution**	**2**	**8**	**4.6**	**R**	**PU**	**30**	**100**	**30**
D8	Symposium in Albania	2	8	1.5	O	PU	16	100	16
D9	Database of companies using chloralkali electrolysis process	3	6	9.0	O	PU	12	100	12
D10	**Assessment report on waste water clean-up alternatives**	**3**	**6**	**5.0**	**R**	**PU**	**30**	**100**	**34**
D11	**Report on treatability study using microbiological methods**	**3**	**6**	**3.1**	**R**	**RE**	**24**	**100**	**36**
D12	Meeting with chloralkali industries	3	6	1.5	O	RE	12	100	9
D13	Database on mercury emissions from coal fired power plants & municipal waste incinerators	4	3	9.5	O	PU	12	100	16
D14	Assessment of control options for mercury	4	3	1.6	R	PU	24	100	25
D15	**Case study report on coal fired power plants etc.**	**4**	**3**	**1.0**	**R**	**PU**	**30**	**100**	**36**
D16	**Workshop in England**	**4**	**3**	**1.5**	**O**	**RE**	**30**	**100**	**36**
D17	Summary report on mercury in oil and gas industries	5	7	4.0	R	PU	12	100	15
D18	Report on biotechnological options in oil and gas industries, including costs	5	7	3,6	R	PU	24	100	27
D20	**Case study at Naftaplin, gas treatment facility, Croatia**	**5**	**7**	**5,0**	**R**	**RE**	**24**	**100**	**36**
D24	Process routes for different case studies	6	2	10.0	R	RE	30	100	12
D25	**Optimum reactor designs for biotransformations**	**6**	**2**	**4.0**	**R**	**RE**	**36**	**100**	**36**
D26	**Complete process design and cost evaluation**	**6**	**2**	**4.0**	**R**	**RE**	**36**	**100**	**36**
D27	**BIOMERCURY database and website**	**7**	**1**	**5.0**	**O**	**PU**	**36**	**100**	**36**
D28	**Comprehensive reports on treatability studies**	**7**	**1**	**5.0**	**R**	**RE**	**36**	**100**	**36**
D29	**Report on longterm performance of industrial bioreactor**	**7**	**1**	**2.0**	**R**	**CO**	**36**	**100**	**36**
D30	BIOMERCURY session at 7th Int. Conf. on Mercury …	7	1	2.0	O	PU	36	100	7
D31	**Project proposals**	**7**	**1**	**4.0**	**O**	**RE**	**36**	**100**	**36**
D32	**Technology transfer agreements, patents**	**7**	**1**	**1.0**	**O**	**CO**	**36**	**100**	**36**
D33	**Preparation of Project meetings**	**8**	**1**	**1.0**	**O**	**CO**	**every 6 m.**	**100**	**every 6 m.**
D34	**Protocols of Project meetings**	**8**	**1**	**0.5**	**R**	**CO**	**every 6 m.**	**100**	**every 6 m.**
D37	**Report to the European Comission**	**8**	**1**	**1.0**	**R**	**CO**	**every 6 m.**	**100**	**every 6 m.**
D38	Project website	8	1	0.5	O	PU	3	100	3
Additional deliverables									
D39	Industrial Area North Coast of Colombia and Chloralkali Plant, Cartagena, Columbia	1	10	0.5	R	PU	n.a.	100	18
D40	Land use change and Hg remobilisation in the Amazon	1	11	0.5	R	PU	n.a.	100	18
D41	**Microbial Mercury remediation as Best Available Technology**	**3**	**1**	**1.0**	**R**	**PU**	**n.a.**	**100**	**36**

Appendix

Case Study 1: Industrial Area, Pavlodar, Kazakhstan

Case Study 2: Former Chloralkali Plant in Vlora, Albania

Case Study 4: Coal Fired Power Plants and Municipal Waste Incinerators

Case Study 5: Naftaplin, Gas Treatment Facility, Croatia

SPECIFIC SUPPORT ACTION

BIOMERCURY

Worldwide remediation of mercury hazards through biotechnology

NMP2-CT-2004-505561

Priority 3 NMP: Nanotechnology and nanosciences, knowledge based multifunctional materials, new production processes and devices

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Deliverable D3

Case study report on Pavlodar site

Deliverable due date: PM 30
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Almaty Institute of Power Engineering and Telecommunications (AIPET), Almaty, Kazakhstan

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PU	Public	✓
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

Case Study Report
Industrial Area, Pavlodar, Kazakhstan

1. Background/Introduction

1.1. History of Pavlodar Chemical Plant

The design statement for the construction of the Pavlodar Chemical Complex (later it was renamed as Pavlodar Chemical Plant (PCP), PO "Khimprom" Pavlodar, JSC "Khimprom", JSC "PCP", JSC "Kaustik") was worked out in 1962 and approved by Decree of National Economy Supreme Committee of Council of Ministers of USSR #286-p /1/. According to the design statement the projected capacity was planed as much as 120 thousand tons of caustic soda /2/, 90 thousand tons of liquid chlorine /1/. The construction of PCP started in 1965 and proceeded till 1992.

The first production – a mechanical-repair shop was commissioned in 1970, a nitrogen-oxygen plant - in 1972, a shop of aluminum chloride - in June 1973. According to the factory design it was planned to produce chemical weapon in the Site #2 which construction started simultaneously with Site #1 700 m to the east /3/.

Location of PCP which is 9 km to the north of residential area of Pavlodar and 5 km to the east of the Irtysh River (fig.1) was chosen due to the number of reasons: proximity of electricity source – coal from coal open-pit mine of Ekibastuz coal fields, fresh water, salt lakes and salt-works, developed transport infrastructure, climatic conditions for evaporation ponds operation and the construction of Pavlodar Oil-Refinery (POR) in the neighborhood where it was supposed to refine west-Siberian oil.

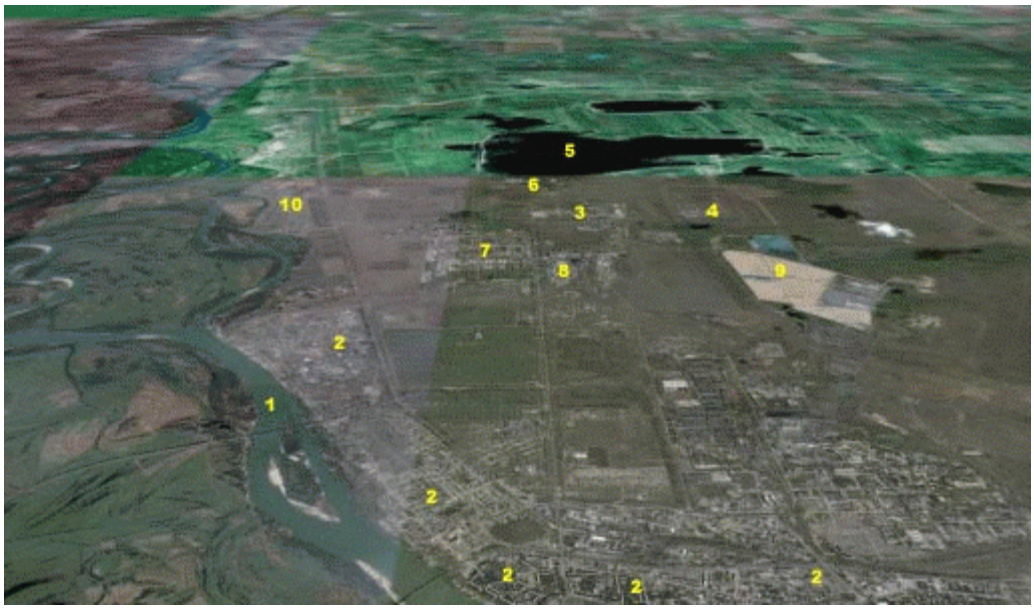

Fig.1. Northern industrial area of Pavlodar (satellite image): 1 – Irtysh River, 2 – residential area of the city, 3 – Industrial site #1 of PCP, 4 - Industrial site #2 of PCP, 5 – wastewater storage pond –Lake Balkyldak, 6 – mercury waste lagoons, 7 - Pavlodar Oil Refinery, 8 – power station TES-3, 9 – ash lagoon of power stations TES-2 and TES-3, 10 – Pavlodarskoe village

In 1970s both these plants PCP and POR and also designed Albuminous-Vitamin Production as well as Plastic Mass Manufacturing Plant were called as a Pavlodar Oil-Chemistry Complex. It was planned that POR would provide PCP and other factories with hydrocarbons row material

which would give an opportunity for PCP to utilize the excess of chlorine obtained while caustic soda production with electrolysis method. Construction of full scale design PCP and POR was not accomplished and Albuminous-Vitamin Production and Plastic Mass Manufacturing Plant haven't even been started because of the USSR collapse. In 1991 PCP covered the area of 2500 hectares (according to the design statement – 132 hectares /2/), and employees staff amounted 6500 people, including 500 engineers (in the design statement it is 8368 including 3271 in weapon production /2/). Additionally to the main production PCP had its own an agricultural farm, well developed social infrastructure and provided the city government with a significant assistance in civilian construction.

At that time of planned soviet economy further development of PCP was restricted by a number of unfavorable factors such as delay in construction of oil-pipe line Omsk-Pavlodar-Chimkent-Tchardzhou and POR. The latter was caused by the construction in neighboring Russian oblast bigger Omsk Oil-Rrefinery. Other factors were: low quality of the halite material – brine from Lake Maraldy which later was replaced with sodium chloride from Baskunchak salt-works in Volga region (Russia), and the lack of experienced force in new developing industrial region. PCP constantly faced the problem of chlorine excess resulting in frequent stoppage of the production. These factors brought the plant to the condition of high accident rate of chemical-technology processes, environment contamination with chlorine and mercury in the long run it influenced the destiny of the plant. Neither participation of PCP in All-Union Association Soyuzorgsintez of the USSR Ministry of chemical industry which controlled the chemical weapon production nor being within the list of 100 defense industrial factories of the USSR which had priority in their construction, helped PCP to develop without crises /3/.

Industrial Site #1 consisted of 30 shops where wide range of products and commodities was manufactured such as caustic soda, chlorine, sodium hypo chloride, ammonium chloride, additives to lubricating oil and engine oils, floto-reagents, anti-freezes, anti-icer, disinfectants and bleaching agents, plasticizers for plastic mass production, phenol-formaldehyde resin, some types of plastic and plastic goods. These products were delivered to industrial plants of the whole Soviet Union, including Kazakhstan, Russia, Byelorussia, Uzbekistan and Kyrgyzstan. At Site #1 one of shops produced defense products – $AlCl_3$ including one of high rate rectification starting since 1977. This product was used for production of missiles SS-20 fuel and thermo isolating coating for a space shuttle "Buran"/3/.

PCP was the last of big chemical plants to be constructed and in case of emergency it can be converted easily into only military production manufacturing mostly binary nerve agents which were developed in the Soviet Union in the 1980s.

Although PCP manufactured precursor chemicals for chemical weapon agents, it has never produced chemical weapon. Since the early 1980s the construction of Site #2 went very quickly where since 1990 production of phosphorus trichloride – initial material for organic synthesis of nerve agents was started. However the construction of technological lines for weapon manufacturing was not accomplished. In 1987 the USSR ratified the Convention on chemical weapon ban and the USSR Government stopped the Program of chemical weapons.

Site #2 was located at separated paled area of 550 hectares in the eastern part of the plant and was designed only for chemical weapon production. It had more strict security and secrecy system than PCP itself and consisted of 5 buildings including main chemical production lines, laboratory plants and equipment for war-sells filling with the chemical agents. By the order of Mikhail Gorbachev, President of USSR construction of the weapon production lines at PCP was not only stopped but dismantling of already installed equipment and buildings was undertaken. Part of the equipment was converted to produce civilian goods.

In 1993 after the termination of caustic and chlorine production which was the basic production of PCP only those shops survived that produced household chemical goods and commodity and reagents for ore mining and processing and energy industries. Part of these productions was privatized in 1994 during establishment of JSC "Khimprom" at that they used their facilities on

the condition of rent. 90% of JSC "Khimprom"shares belonged to the state. The most standing idle equipment subject to any value were sold in order to pay to minimum working staff and to cover the debts. The exception was the defence equipment which were protected by Soviet-American non-proliferation treaty dated 1989, ratified later also by the Kazakhstan Government. However Kazakhstan did not include PCP into the list of the plants producing chemical weapon. Soon after closing of chlor-alkali production it became obvious that PCP will not be able to be kept as one indivisible technological complex. Meanwhile potential investors of new chlor-alkali production were scared about the presence of mercury hot spot in the Site #1 the elimination of which required additional overproduction cost. Therefore since mid-90s plant management and local government focussed on demercurization activity and search of funds. In late 1998 JSC "Khimprom" started demolition of the most mercury contaminated structures in Shop 31 at the own and oblast budget cost in order to continue this work in 1999 at the cost of state budget. However after the demolition of roof and some walls of Shop 31 the funding was stopped and the next spring (April 1999) local government declared situation of emergency which was caused by threat of intensive evaporation of spilt mercury. This event attracted attention of mass media and environmental movement. Under their pressure the state government had to allocate money for collection of spilt mercury, dismantling of the equipment and part of the building 31. On 26.04.1999 JSC "PCP" was segregated from JSC "Khimprom" so that it has opportunity to receive funds from the state budget and to conduct demercurization works in Shop 31. However on completion of 1999 the funding was stopped again. Since 09.01.2001 JSC "PCP" was assigned to communal property of Pavlodar oblast administration.

Demercurization works at the cost of republican budget were resumed by JSC "PCP" only in early 2002. By 2005 the first Phase of demercurization project was accomplished. In 2006 JSC "PCP" was proclaimed a bankrupt and its property was put for a bid while the territory where demericurization works were held was withdrawn from the bid lot and still is a communal property. New chlor-alkali production (with membrane method) will be revived by JSC "Kaustik" with private capital. JSC "Kaustik" was established in 2004 based on only private capital and had purchased the half of the property of PCP industrial site #1.

1.2. Chlor-alkali production. History of the pollution problem in Pavlodar /4-8/

Production #3 manufactured chlorine and caustic soda (NaOH) since 1975 till 1993 by electrolysis method where mercury was used as a cathode. There were 80 electrolyzers (CDM 150-7.3) installed in shop #31 (in 1975 - 72 electrolyzers, in 1984 - additionally 8 electrolyzers, and after full repair in 1986 there were 68 electrolyzers totally). The capacity of production amounted 112700 ton of caustic soda and 100000 ton of chlorine per year. Raw materials sources: sodium chloride - from Baskunchak (Volgograd oblast, Russia), water – from the Irtysh River.

Horizontal electrolyzer CDM 150-7.3 made in GDR (with maximal load of 150 kA, cathode current density of 7.3 kA/m^2, length of 14.5 m, width of 2.03 m, number of anodes – 120) with mercury cathode (20.4 m^2) and vertical amalgam decomposer (with diameter of 1.0 m in upper part and 1.44 m in lower part, height without fridge – 2.07 m), produced gaseous chlorine and hydrogen as well as chlorides free aqueous solution of sodium hydroxide. Due to mercury the electrolysis of sodium chloride aqueous solution

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2\uparrow + H_2\uparrow,$$

was divided into two electrochemical processes:
in the electrolyzer gaseous chlorine was generated on graphite anode and sodium amalgam - on mercury cathode

$$2Na^+ + 2Cl^- + (Hg) \rightarrow 2Na\,(Hg) + Cl_2\uparrow,$$

and in the decomposer both aqueous solution of sodium hydroxide and gaseous hydrogen were generated on the surface of a graphit extension as a result of interaction of sodium amalgam with water

$$2Na\,(Hg) + 2H_2O \rightarrow (Hg) + 2NaOH + H_2\uparrow.$$

Technologically the process of sodium hydroxide production looked like a travel of depleted sodium amalgam (with sodium concentration ≤ 0.005%) from the lower part of the decomposer upward to the electrolyzer inlet with the help of mercury pump, followed by the saturation of amalgam with sodium under the current up to concentration 0.45 % during its move along sloping bottom of the electrolyzer, entering 0.45% of sodium amalgam from the electrolyzer in the upper part of decomposer and the formation of NaOH in the process of interaction of sodium with desalted water on the graphite extension at trickling of amalgam down along decomposer with lowering concentration from 0.45 to 0.005%. NaCl brine flowed forward with amalgam in the electrolyzer while NaOH solution contra flowed to amalgam in decomposer. Concentration of NaCl in brine at the electrolyzer inlet was 300-310 g/l, in anolyte outlet - 265-275 g/l (anolyte contained dissolved 0.3-0.5 g/l chlorine). Alkali solution concentration at the electrolyzer outlet was 43-46%.

Electrolysis brine was prepared with anolyte additional saturation in the Shop # 34a where it was stored in two horizontal rubberized tanks of 80 m3 each. From them brine drifted in Shop # 31. Anolyte entered in two titanium tanks of 40 m3 each and pumped out to Production # 2 for the following dechlorination and returned later to Shop 34a.

Solutions temperature in the electrolyzer reached 80-85^{o}C, and in decomposer – 80-100^{o}C. High temperature caused contamination with mercury of all electrolysis products and wastes: anolyte NaCl depleted solution, solution of alkali and hydrogen. Alkali was contaminated with elementary atomic-dispersed mercury; anolyte, chlorine and exhaust gases contained water dissolved mercuric chloride; hydrogen and output ventilation gases – gaseous mercury. In the long period of electrolyzers operation a lot of mercury was sludged with the formation of amalgam oil which was hand-removed regularly from electrolyzer's accumulating pockets. For amalgam cleaning the accumulating pockets were rinsed with purified water.

Alkali solution was cooled, separated from mercury and other admixtures by filtering through frame filters FP-50 and afterwards alkali was passed for either storage or being poured into tanks. Hydrogen was cooled to 20-25^{o}C immediately above the decomposer so that the most condensable mercury returned in decomposer. Afterwards hydrogen was cooled again to 15-20^{o}C with the return of condensed mercury in electrolyzers, and mercury removal with chlorinated water took place. Remaining chlorine was absorbed from hydrogen with alkali solution (with NaOH concentration of 180-240 g/l), then purified hydrogen was rinsed with water, diluted with nitrogen and emitted into the air. Mercury content in emitted gases shouldn't had exceeded 0.01 mg/m^3. In winter period however hydrogen was emitted into air skipping purification stage. Received in electrolyzers chlorine-gas with concentration $Cl_2 \geq 90\%$ and admixture of H_2 gas ≤ 1% was constantly pumped out in collector so that to maintain vacuum of 5-10 mm of a water column. Humid chlorine-gas was washed with recycle water (mainly for NaCl and Hg removal), cooled and dried off with concentrated sulphur acid in two parallel systems of cooling and drying. Then it was compressed and routed down to Building 36 of Shop # 4. Analyte prior to additional saturation with NaCl was dechlorinated by acidification and addition of sodium sulphide with following removal of sludge containing mercury sulphide, HgS using press-filter. Regulated content of mercuric chloride in anolyte at the cells outlets – 0.002%, while in purified brine at inlet – 0.001%. Exhaust gases generated by anolyte in drying and pumping section as well as chlorine-gas from the cells operating with low load have been pumped out to ejector to

be neutralized. Chlorine and mercury have been absorbed with the solution of alkali with NaOH concentration of 180-240 g/l, which circulated through the ejector until alkali concentration dropped to 20 g/l. Purified exhaust gases were emitted into air. Ventilation gases were emitted in the air without treatment. All washing and absorbing solutions as well as mercury containing water were discharged into mercury sewage. Regulated norm of mercury containing wastewater at chlor-alkali production amounted 15 m^3/day. Liquid mercury sludge was settled, mercury was returned in the cells. Not settled sludge was diluted with water in the tank where sludge was washed up with stirrer and metallic mercury regenerated for 3 hours. Regenerated mercury was returned in the cells and not settled sludge was subjected to thermal regeneration. Solid mercury sludge formed while anolyte purification process and containing mercury sulphide were routed to burial place in the west cell (#1) of evaporation ponds and sludge formed while alkali purification process and containing metallic mercury – to thermal regeneration. Graphite from worked-out anodes, khlorin fabric and filter glass-fiber were also mercury bearing wastes. These wastes were buried at a special landfill for solid wastes. Electrolyzers underwent regular full repair in the mechanical repair shop where humin worn-out coating had been thermally annealed and replaced with new coating.

Mercury that had been lost during the electrolyzers operation as a result of leakage and during repair was washed out with water from the electrolysis shop's floor into the floor troughs and further into settling pits of mercury contaminated wastewater sewerage. Troughs and settling pits were periodically cleaned off using portable titanium vacuum tank one of connecting pipes of which was connected to vacuum line and another was connected to rubber hose with the help of which mercury was collected. Collected mercury returned to the electrolyzers. The floor of electrolysis shop was covered with special coating which was replaced several times for all time of its operation.

The plant of mercury sludge thermal regeneration was launched in 1980 with capacity of 150 m^3/year and reached the capacity as much as 48 m^3/year. The plant consisted of 3 induction furnaces of periodic activity. Each furnace had four cylinder baskets with welded bottom. Heavily contaminated sludge (4-15%) was mixed manually with sawdust and limestone in the ratio of 20:1:1 and loaded manually in the baskets. The baskets were placed in the furnaces with the vacuum rate of 0.2 kgc/cm^2. Heating was proceeded by stages for 14-15 hours till the maximal temperature 550-600^oC. For mercury vapor condensation a vertical heat-exchanger with water casing and heat exchange area of 17 m^2 were used. Exhaust was cleaned additionally either in adsorbers (there were 2 plants: operating one and reserve one) filled with the coal HPK-3P or in the vertical cylinder tanks with capacity of 2 m^2 with a stir, bubbling it through 10-20% Na_2S solution layer. Mercury bearing wastes from this plant represented cinder and sludge (buried in the evaporation ponds), wastewater (to be discharged into mercury wastes sewerage) and cleaned exhausts and ventilation gases (to be emitted in the air).

Wastewater sulfide treatment was located in the buildings 40, 40a und 40b. This treatment plant was launched in 1975 simultaneously with chlor-alkali production. Treatment process consisted of pH correction of mercury bearing wastewater, settling of primary mercury sludge, mercury oxidizing up to Hg (II) by chlorine followed by removal of chlorine excess, second correction of pH and Hg (II) precipitation from solution with the help of sodium sulfide. Poorly soluble mercury sulfide (II) was settled with iron sulfate as a coagulant with following continuous settling of mercury sludge. Treated effluents were collected in the tank 40d of 5000 m^3 capacity. After filling 40d tank with wastewater they were discharged into the wastewater storage pond Balkyldak only if the sanitary laboratory found the mercury level there to be safe.

There were some major technological drawbacks of sulfide method: low rate of mercury sulfide sediment formation, by-processes of soluble poly-sulfides formation and hardships of solid phase separation. Therefore mercury concentration in wastewater discharged from 40d tank in the wastewater storage pond did not meet the standards very often. Besides Production # 3 discharged illegally wastewater to the pond Balkyldak avoiding sulfide clean-up very often. It forced the management of PCP to reconstruct the system of wastewater collection and treatment.

In 1978 sulfide based treatment plant was replaced with the facility based on the ion-exchange however it was operated not regularly. Achieved capacity reached 30 m^3/hour. Wastewater were filtered, acidified to pH 1-3 and chlorinated in a chlorinator at active chlorine concentration of 0.1 – 0.8 g/l in the water for clarified water and up to 2 g/l concentration for non clarified water. Then chlorinated water was filtered again, de-chlorinated through adsorber filled with ARV charcoal of 2.5 m layer, filtered again and run through 4 adsorbers cascade filled with anion-exchange resin VP-1-AP. The resin and charcoal were loaded to the adsorbers from the top and unloaded from the bottom onto screen-tray while the wastewater went from the bottom upwards to be treated. Worked-out resin and charcoal went for regeneration and poor mercury sludge – to mercury factory. After adsorbers wastewater became subacid therefore it was neutralized with alkali up to pH 7 and discharged in the eastern part of the special evaporation ponds (#3). Approved limit of wastewater clean up was 0.005 mg/l. During the stoppage of anion–exchange treatment plant mercury bearing wastewater of chlor-alkali production were discharged in the evaporation ponds without treatment.

Evaporation ponds – special engineering testing ponds - were constructed in 1976. Their design capacity was 200 m^3/day or 73000 m^3/year of mercury containing effluents. Evaporation ponds are located 1.5 km to the north of Site # 1 of PCP on the south shore of the pond Balkyldak. They consisted of 3 ponds of 344x200 m each, with dam height – 3 m, mean depth of each pond - 2 m, capacity 115000 m^3 each and the total water surface – 18.3 hectares. Bottom of these ponds represents rolled ground covered with special screen. This screen consists of two layers of stabilized polyethylene film 0.2 mm thick and three sand layers 1 m of total thickness. According to the design two ponds were expected to be involved in the accumulation process and the third one as an emergency pond. However in the operating process mainly eastern pond (#3) was used as the evaporation pond, middle pond (#2) was used as an emergency and western one (#1) - as a solid wastes disposal (mainly for graphite and sludge from anolyte).

After the completion of special evaporation ponds construction and mercury sewage systems re-construction unapproved discharge of mercury contaminated wastewater from chlor-alkali production into the general PCP's sewage systems going to the pond Balkyldak became technologically impossible. Communication between Production #3 and the whole plant was disconnected. The anion–exchange treatment plant was connected with the evaporation ponds via above-ground sewage system for mercury contaminated wastewater – pipes made of titanium.

Wastewater storage pond - Lake Balkyldak is located 5.5 km to the east from the Irtysh River flood-plane. According to the initial design of 1975 it had a designed capacity of 56.92 millionm^3, the surface area of 15.9 km^2, evaporation rate of 9.6 million m^3 at critical level of 109.0 m and according to the design of 1985 after dams build-up it has designed capacity of 74.0 million m^3, surface area of 18.0 km^2 and evaporation rate of 11.4 million. m^3 at critical level of 110.8 m. The territory of Lake Balkyldak was assigned to PCP for the construction of a storage pond-evaporator for the industrial wastewater discharge by Decree # 48p of Council of Ministers of KazSSR dated January 20, 1969. That time level of the water surface was at the mark of 105.11 m (25.10.1971). The operation of the wastewater storage pond was started in 1971 without any nature protection measures. Later the pond was confined by two fixed ground dams 8425 m long (eastern und western sides) and surrounded from north, west and east by the anti-filtration screen of "cut-off wall" type 0.6 m thick and 2.5-6.0 m deep. However in several depression sectors of cut-off wall was constructed either without pioneer dam or was not constructed at all. It brought to the penetration of the pond's surface water along depressions in relief toward the villages Pavlodarskoye, Alekseyevka and resort Muyaldy up to 2-3 km long /9/. Until 1978 the pond Balkyldak received wastewater of the whole North industrial zone of Pavlodar (as of 1978: PCP – 4.3 million m^3/year, tractor manufacturing plant – 3.9 million m^3/year, cardboard-ruberoid factory – 5.6 million m^3/year and POR – 1.5 million m^3/year and power plant TES-2 – 0.4 and power plant TES-3 -0.1 million m^3/year, totally - 13.31 million m^3/year /10/). Later it was assigned to PCP but had to receive seasonal run-off and drainage water of joint ash lagoon of power plants TES-2 and TES-3 (this ash lagoon still represents the main source of the

pond Balkyldak recharge with groundwater) along with PCP own wastewater. But actually in 1988 the volume of PCP discharged water into the pond amounted 6-8 thousand m³/day, tractor manufacture's – 2.0 thousand m³/day, TES-2 and TES-3 – 2.0 thousand m³/day (mean daily data) with limit of 5 thousand m³/day approved by the Pavlodar oblast government in 1986 /9/. The maximal level of water in the pond Balkyldak was reported to be 110.95 m on 18.05.1994.

Approved load of metal mercury for one electrolyzer was 2750 kg, i.e. totally there was 220 ton of mercury in electrolyses cells. According to data /11/ since 1975 till 1989 for 14 years of production 685525 ton of caustic soda was produced with 1089.356 ton mercury used.

The balance of major mercury technical losses was following: 0.8% of the losses fell at sludge accumulated and treated during production process; up to 1.9% - vent emissions, up to 2.6% - sludge sent to mercury factory, up to 3.9% - atmospheric emissions with hydrogen, up to 11.8% - wastewater and solid sludge transported to the ponds for solid and liquid mercury wastes, up to 83.7% - unaccounted losses. The latter were caused by spills and leakage of metallic mercury and its not full collection during operation and repair of the electrolyzers.

According to the messages of the former PCP managers /12-13/ it is evident that in 1990-1993 (last period of chlor-alkali production) about 200000 tons of caustic soda was produced and more then 175 tons of mercury was utilized. Totally about 2.6% of used mercury was sent for treatment as sludge /11/, i.e. 33 tons. Former the plant managers also informed /12-13/, that after chlorine production stoppage and the following building and equipment dismantling (Shop # 31) about 140 tons of metallic mercury was either poured out of equipment, collected from floors or thermally extracted from sludge and sent to a mercury factory. Thus the total loss of mercury during the whole chlor-alkali production process can be estimated as high as **1310 tons**, 1100 tons of which were unaccounted losses accumulated in the concrete floor and grounds under the Shop # 31 and its proximity. Chemically aggressive medium there caused quick deterioration of the equipment of the chlor-alkali production. Electrolyses shop had a higher then common accident rate because at the period of chlorine overproduction and filling of all existing tanks with this gas the electrolyzers were either de-energized or transferred to a lower current load. This adversely affected electrolyzers' technical status. In 1986 Production #3 of PCP underwent a scheduled capital repair. In 1988 Program of conversion of technology based on mercury method which was used at electrolysis plants into membrane technology was accepted in the USSR (in 1994 this program was stopped due to the Soviet Union collapse). Since 1990 the construction of new membrane electrolysis shop was started at PCP near the building # 34. That shop was expected to replace Shop # 31. Main infrastructure of the Production #3 was supposed to be kept as it was. The construction of the new shop distracted the funds from the current repair and reconstruction of building # 31. Unsatisfactory technical condition of chlor-alkali production resulted in the Resolution of the USSR chief sanitary doctor "On a ban of chlor-alkali production at Pavlodar plant "Khimprom" № 89-35 dated 12.07.89. However the production of chlorine and alkali was intermittently continued and lasted for some more years. Production #3 was finally stopped after the USSR collapse by the resolution of Plant director B. Sharov /13/ in August 1993 after it was found out that the building #3 roof began destroying because of corrosion and some components of building structures started falling down into the hall of the electrolysis plant. In January 1994 Ministry Cabinet of the Republic of Kazakhstan issued a Decree № 7 "On measures for improvement of environmental and sanitary situation in Pavlodar industrial region" that gave up any hopes for the revival of chlor-alkali production based on the mercury electrolysis. This Decree allowed the equipment and materials which were not used in the production any more to be sold out. Disassembling of expensive equipment and structures made of non-ferrous metals took place in 1994-1995.

The following years PCP management and local authorities were attempting to revive chlor-alkali production in Pavlodar on the base of progressive membrane technology. In 2004 in the former PCP territory new JSC "Kaustik" was established which at present carries on talks with foreign companies on the procurement of western technology and equipment for creation of new membrane based chlor-alkali production.

2. Assessment of pollution problem

2.1 Pollution localization and extension

Systematic survey of the mercury pollution extension at the area of PCP and risk assessment was carried out in 1989-2002 by four phases: in 1989-1990, soviet period in compliance with the following documents: "Measures on solution findings of environmental rehabilitation of the territories contaminated with mercury to be taken during the shutdown of mercury electrolysis based production and its replacement with membrane technology in Pavlodar PO "Khimprom" approved by USSR Ministry of Chemical Industry dated 31.12.88 and the Decree № 89-35 of USSR Chief sanitary doctor "On ban of chlor-alkali production at Pavlodar PO "Khimprom" dated 12.07.89 /11, 14-18/, in 1990-1993 in the framework of PO "Khimprom", Pavlodar Environment Impact Assessment /19-24/, in 1997-1998 on the project INTAS-Kz 95-19 funded by European Union /25/ and in 2001-2002 on the project INCO-2 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" ("Toxicmanagement") also funded by European Union /26-27/.

First study was conducted by JV "Evrohim", Kiev an author of Demercurization Design and Pavlodar Hydrogeological Expedition – Science and Technology Centre "Technolog" (PHH) being a sub-contractor of JV Evrohim. The study was limited to the west part of Industrial Site #1 of PCP and mainly related to mercury contaminated soils and groundwater around the Building 31, where electrolysis of sodium chloride solution was carried out. The situation analysis and balance calculation of loses according to historical documents being in PCP and PHH archives were conducted as well as field study of soils and groundwater including drilling of boreholes and digging pits including inside the building itself. The main disadvantage of the study was low quality of both groundwater sampling and analytical works that rather lead to overstating of mercury concentration in water samples. In the former USSR overwhelming number of hydrogeological studies on environmental control had similar disadvantage in 1980s-1990s.

Main results the balance and hydro-geological investigation of chlor-alkali production at PCP were as follows:

- estimated mass of mercury lost since 1975 till 1989 during the operation of chlor-alkali production is 1089 tons including 14 - 63 tons with hydrogen and vent exhausts,
- deposited in floor and grounds under the electrolysis factory, the Building 31 – 813- 866 tons,
- dispersed in the area adjacent to the Production #3, along the roads, place for storage of wastes and contaminated equipment - 42-45 tons,
- deposited in sludge of the special evaporation ponds (cell #1) – up to 137 tons,
- deposited in sediments and water of Lake Balkyldak - 10-15 tons,
- accumulated in water of evaporation ponds (cells #2, 3) – 1-2 tons;
- main hot spot of mercury contamination is located in the territory of electrolysis shop 31 and has an area of 7519 m^2, where about 1131.8 tons of mercury is contained in 22 thousand $м^3$ of contaminated material including concrete floor of electrolysis factory – 104.1 tons, suspension grounds – 859.1 tons, bottom clays – 6.4 tons. Depth of metal mercury penetration exceeds 3 m. However main amount of mercury (about 99%) is accumulated on the surface of undisturbed ground which is not deeper than 2 m from the floor;
- area of mercury contaminated soils in the Site #1 is as much as 521150 m^2. The most contaminated sector is located eastward of Shop 31. Average concentration of mercury in the topsoil of 0-0.25 m deep in the contaminated area reaches 2-14 mg/kg. Total amount of mercury dispersed in the topsoil of 0-0.25 m deep is about 2.8 tons, total amount of contaminated ground here is about 208000 tons. Mercury penetrates down to depth of 4 m. However in the depth of

1.5 m mercury concentration does not exceed maximal permissible concentration for soils (MPC_s - 2.1mg/kg). Calculated amount of mercury for the layer of 0-4 m (excluding mercury under the Shop 31) is 10 tons.

- plume of groundwater mercury contamination spreads from Shop 31 west-northwest direction up to 800 m. Total area of groundwater mercury contamination in upper layers is 0.55 km^2. The volume of contaminated water of all horizons was estimated as 2.08 million m^3, which could contain about 10.0 tons of mercury (with concentration of 12.5 – 103.0 mg/l and mineralization of 62-72 g/l) in the form of soluble mercury (II) chloride.

- in two cells (#1, 2) of evaporation ponds there are mercury containing sludge from anolyte clean up. Mercury there represents sparingly soluble mercury sulfide. Mercury contents in this sludge ranges from 0.01 to 0.33%. Totally evaporation ponds accumulated 140 tons of mercury salts.

- in water of the cell for liquid wastes of the special evaporation pond – 1-2 tons of mercury.

- pond Balkyldak received mercury with wastewater discharge. Average mercury concentration in the surface water of the pond reaches 0.01 mg/l, that is 20 times higher then MPC_w. Taking in account the total volume of wastewater legally discharged to Balkyldak and mercury concentration in these wastewater one can estimate the total amount of mercury in water and bottom sediments. It is equal to 10-15 tons;

- hydrogeological forecast of the further mercury underground spread from PCP showed the following rate of mercury movement: in perched groundwater and the first aquifer - 20-46.7 m/year, in the second aquifer - 12-28 m/year and in the third one - 46-56 m/year.

Field studies of 1990-1993 in the framework of Environmental Impact Assessment were performed by Center of Health Protection and Research Institute of New Technologies and Materials at Al-Farabi Kazakh state National University (KazGU). Mainly snow cover and to some degree soils around the industrial site of PCP were investigated in the final period of operation of the chlor-alkali production that makes this information most valuable. Analytical works accompanying these investigations conducted using soviet equipment (atomic-absorption photometer – Rtut' 101) were more correct than hydro-geological ones of 1089-1990 however.

In winter 1990-1991 snow cover of residential area and south part of North industrial area (around industrial sites of radio plant "Vesna" and PO "Pavlodar Tractor Plant") was investigated with regards to mercury contamination. Exceeding MPC_w for mercury in the snow melted water (up to 1.5 μg/L) was found around the gardening cooperative "Khimik". Most likely it was found the south end of the mercury anomaly located to the north from the investigated area. In 1991-1992 the area of interest was extended up to the north border of the PCP industrial site, and besides 45 samples of snow melted water additional 32 samples of soil were taken down to the depth of 50cm. In the gardens of the north suburb 96 samples of fruit and vegetables were taken. Exceeding MPC_w for mercury (up to 2.5 μg/L) was found in snow melted water around PCP over the vast area (southward of Pavlodar Tractor Plant, westward Lake Muyaldy and eastward the Irtysh Riverbed) however there was not found any mercury contamination of soils as well as fruit and vegetables.

Study of 1993 included the sampling of 150 soil samples from 28 boreholes (down to the depth of 2 m) northward of industrial site of PCP (at the area of 500 km^2) and didn't reveal the mercury concentration in soil exceeding 0.5 mg/kg (0.4 MPC_s). In 42 agriculture products and 26 samples of groundwater and surface water taken in the same area mercury presence was not found as well. There was the only exception – one sample from the pond Balkyldak where 0.1 μg/l of total mercury (2 MPC_w) was found.

These field works showed the annual mercury contamination of snow cover coming from atmospheric precipitation did not lead to significant contamination of soils around PCP in early 90s because most likely this way of the mercury contamination spread had short term of existence.

Project INTAS–Kz 95-19 funded by EU was accomplished by the team of "GeoKEN" Ltd. which later became a part of Institute of Natural Science, Almaty (INS). KazGU also took part in the works. The project included two field study of 1997–1998 in the area of more than 1000 km^2 northward of industrial site of PCP that covered area around ponds Balkyldak and Sarymsak as well as floodplain of the Irtysh River. According to the regular grids of 0.7x0.7 km, 1x1 km and 2.8x2.8 km more then 2000 samples of soils were taken from the depth of 0-15, 15-30 and 30-50 cm. From the same area about 100 samples of surface water and 100 samples of bottom sediments were taken. About 600 soil and sediments samples were tested in regards of presence of 7 heavy metals using spectral analysis and all these samples were analyzed for mercury content with atomic–absorption method.

No exceeding of MPC_s for any of heavy metals was found except some cases of mercury presence close to the north boarder of Site #1, as well as close to special evaporation ponds on the shore of the pond Balkyldak. However several hotspots with increased mercury concentration (100 times higher then local background concentration) were found mainly in local depressed areas where snow melted water accumulate in springs. There were also hotspots with increased mercury concentration (not exceeding MPC_s) in soils and bottom sediments of oxbows of the Irtysh River and in shoaling surface water of the Irtysh River and in oxbows water at the level of MPC_w. Such mercury contamination of the Irtysh River floodplain was explained by possible rise of mercury contaminated groundwater up to the surface.

Average level of surface water contamination with mercury in the pond Balkyldak was estimated as 1 µg/l (2 MPC_w).

The project INCO-2 ICA2-CT-2000-10029 "Toxicmanagement" was implemented in 2001-2002 already after demercurization works had been started in the moment of their suspension caused by cessation of their financing. The Kazakhstan partners were BG Chair of Environmental Technology of Almaty Institute of Power Engineering and Telecommunication (AIPET), Institute of Hydrogeology and Hydrophysics (IHH), KazGU and INS. The foreign partners were the Department of Civil Engineering of Southampton University, Great Britain (SU) – the coordinator of the project, Consulting Company "GeoDelf", Netherlands (GeoDelf), JV Evrohim and Siberian Spiritual-Ecological University, Omsk, Russia (SSEU).

Participation of Western Partners enabled both to purchase state-of-the-art analytical equipment, equipment for sampling and GPS and to use up-dated reference materials and methods of sampling and analysis including QA/QC

Investigation of mercury contamination of soil in the territory of PCP and around it (fig.2-7) has allowed revealing some large centers of contamination with mercury concentration which was 500 times more than MPCs for mercury (2.1 mg/kg): four of them were at the territory of the Industrial Site #1 and came from the electrolysis shop 31, the shop of production solutions regeneration, tanks for mercury containing wastewater storage and the building of mercury contaminated wastewater treatment plant; one of them was on the shore of the pond Balkyldak and was connected with special ponds for storage of mercury wastes.

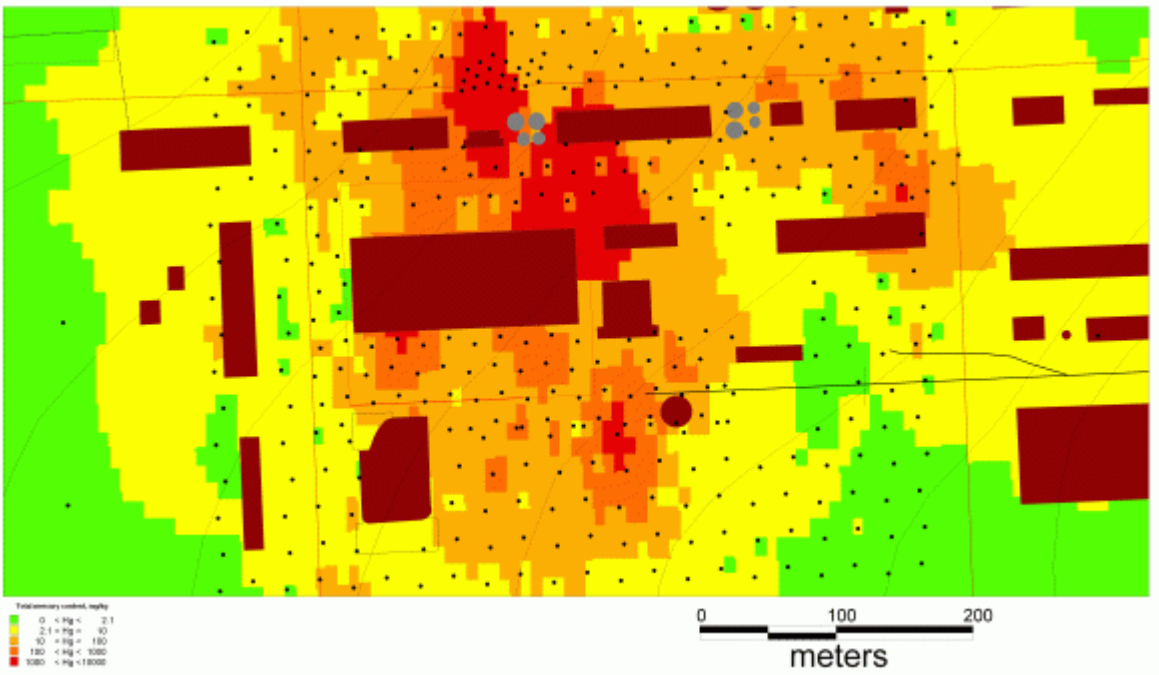

Fig.2. Map of topsoil (0-10 cm layer) mercury contamination at Industrial site # 1 of PCP

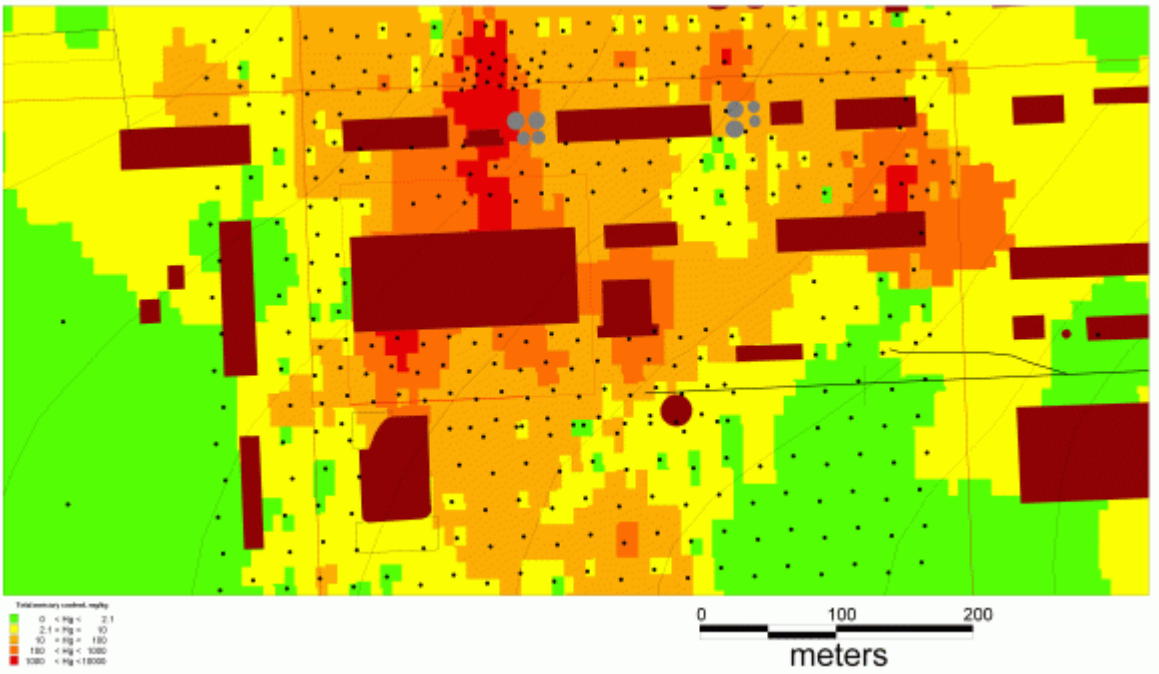

Fig.3. Map of soil (10-20 cm layer) mercury contamination at Industrial site # 1 of PCP

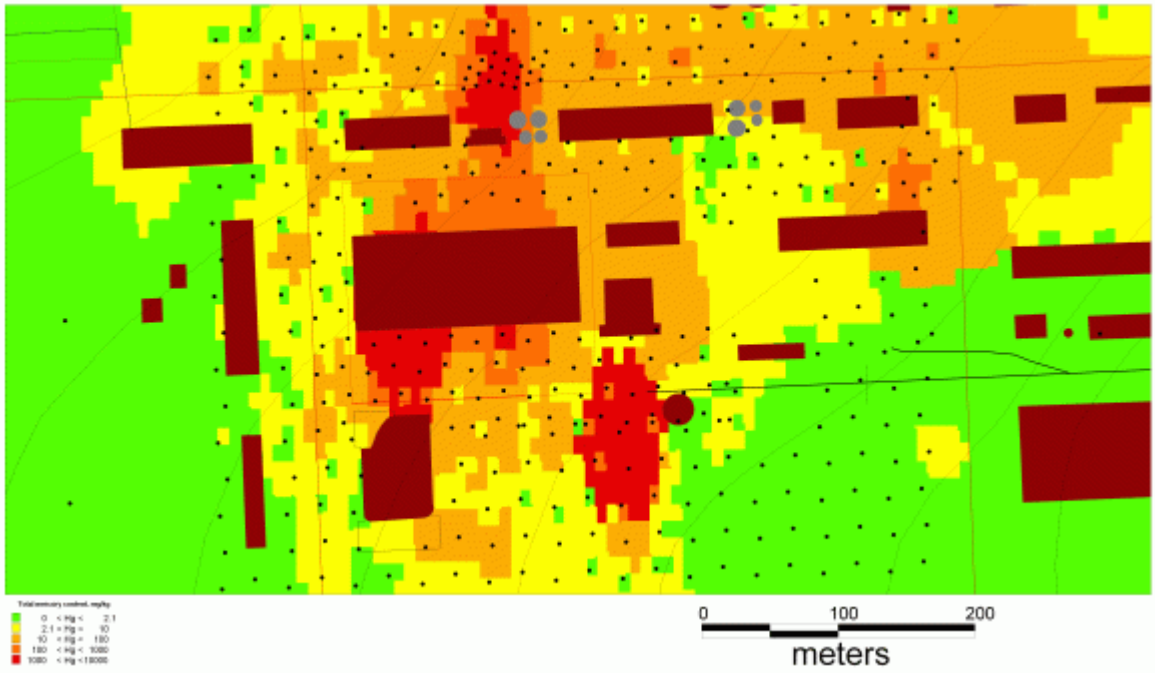

Fig.4. Map of soil (20-50 cm layer) mercury contamination at Industrial site # 1 of PCP

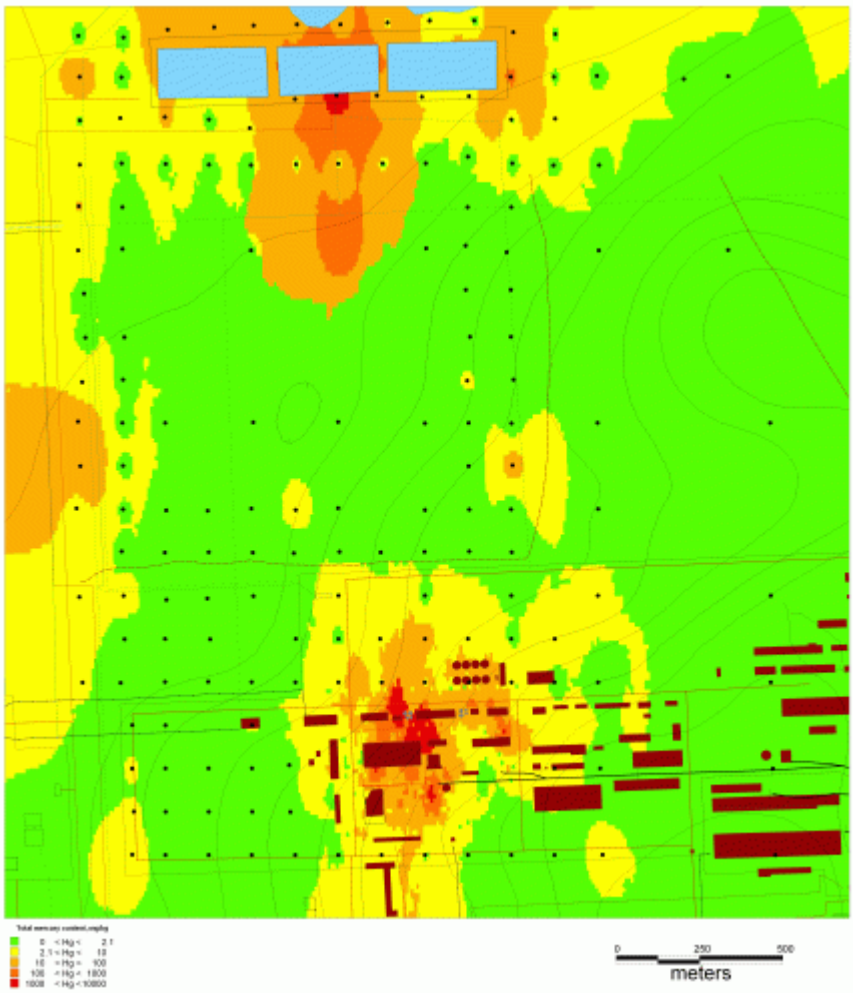

Fig.5. Map of topsoil (0-10 cm layer) mercury contamination around Industrial site # 1 of PCP

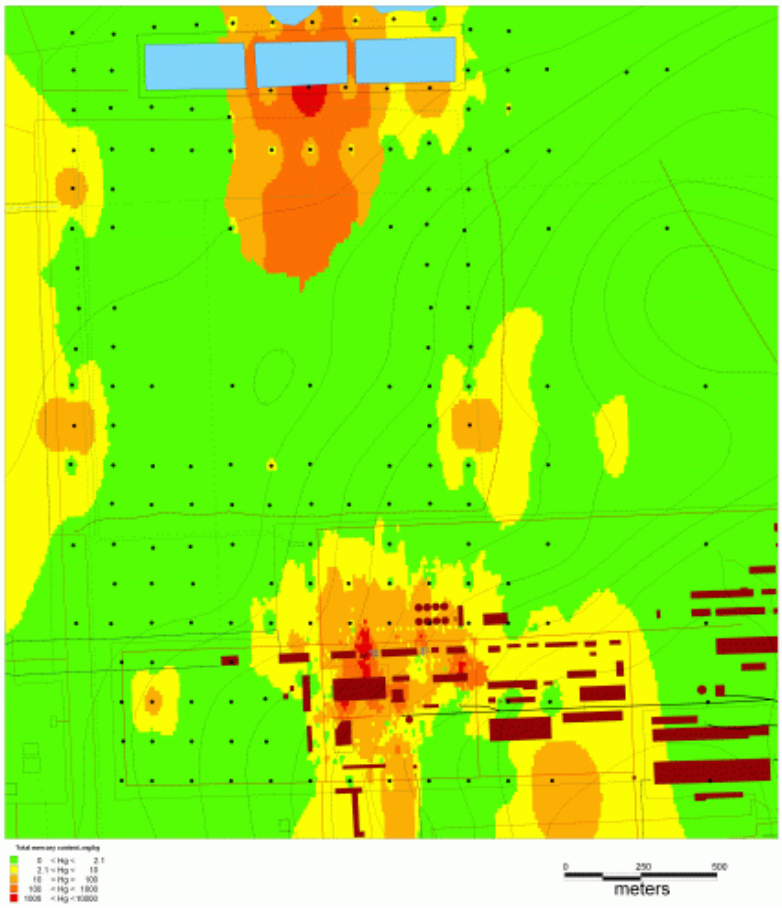

Fig.6. Map of soil (10-20 cm layer) mercury contamination around Industrial site # 1 of PCP

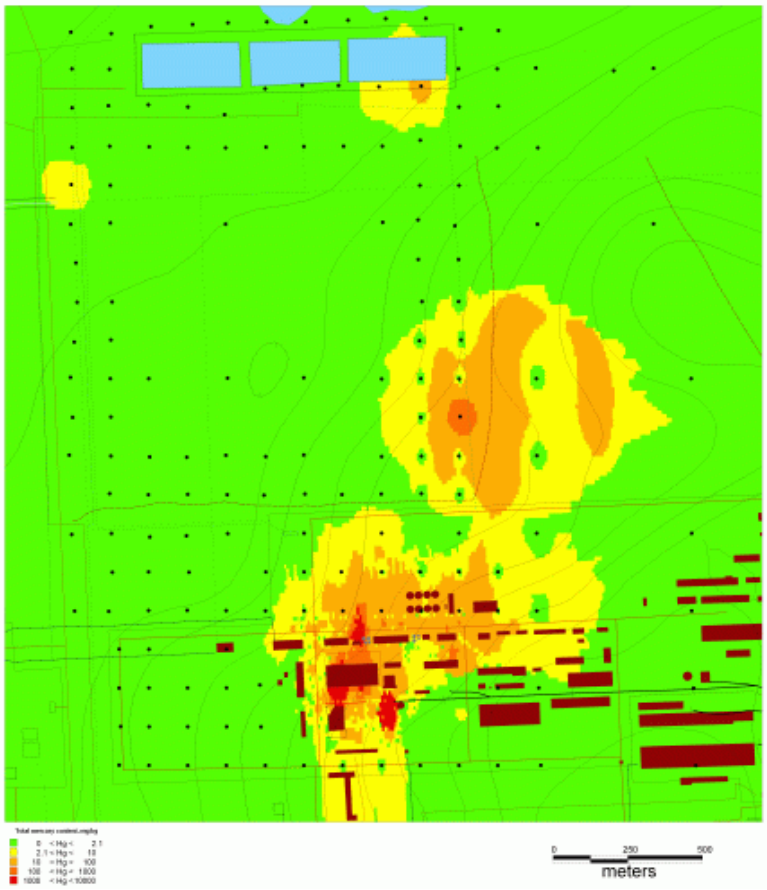

Fig.7. Map of soil (20-50 cm layer) mercury contamination around Industrial site # 1 of PCP

Three mercury hotspots at the territory of Industrial Site #1 were formed by spill of either mercury containing solutions or liquid metal mercury. Their intensity was being changed not very much along the depth of sampling in a soil layer down to 0.5 m. The source near the north-east corner of the Building 31 was at the surface and either was formed at the cost of dispersing mercury containing solid wastes or arose fairly recently during dismantling the equipment. The highest concentration of mercury in ground were found 1.7 m deep both near the electrolysis shop (Building 31) and under its concrete floor slab (tens and hundreds of g/kg). High mercury background concentration (from 1 to 50 of MPCs) in soil layer of 0-50 cm within the area of about 1 km^2 around the former manufacture of chlorine and caustic was bound up with high mobility of mercury forms, which provoke the contamination.

The hearth of soil mercury contamination in the area of the special evaporation ponds was rather shallow and was formed by wind transfer of dispersed solid mercury containing wastes.

The location of one of two (the western one) less intensive hearths of topsoil contamination between the Industrial Site #1 and the special ponds has overlapped a contour of spread of plume of mercury contaminated groundwater and, probably, was caused by their reach of a surface at the cost of evaporation and capillary effects. Second hearth (eastern), probably, was formed by leaking mercury containing wastewater from the sewerage system and their accumulation within this area. This assumption was proved by numerous detection of high concentration of mercury in the borehole 7P (4250 ng/l in 2002) made by different organizations within many years.

Amount of soil and ground in the layer of 0-50 cm polluted higher than 10 mg/kg, and also amount of mercury there were (without mercury deposited under the Building 31), accordingly, 19263 m^3 and 2931 kg for the territory of the Industrial Site #1 of PCP, and 79542 m^3 and 16022 kg for the territory between the wastewater storage pond Balkyldak and the Industrial Site of PCP.

The level of mercury contamination in atmosphere near to the Building 31 in summer time considerably exceeded daily average MPC_{da} (300 ng/m^3) amounting to 25000 ng/m^3 at the cost of metal mercury evaporation from the surface of ground and construction materials and exceeded 100000 ng/m^3 at demercurization works carrying out. Spread of the air pollution was confined by the radius of 200 m around the site of chlorine and caustic soda production and considered as a local threat.

Investigation of existing observation and production boreholes in 2001 showed that the spread of groundwater with mercury contents more than MPC_w (500 ng/l) was confined within the territory of the Industrial Site, places where the sewerage system went and area of the special ponds. Numerous investigation of the borehole 24-91, located 2 km to west from the Building 31 and in water of which it was originally found the mercury concentration of 1564 ng/l (3 MPC_w), showed that this borehole was contaminated with mercury during the previous samplings. In none of water samples selected from production boreholes in village Pavlodarskoe it was revealed mercury more than 7 ng/l (0.014 MPC_w), that practically coincided with the mercury detection limit according to used analytical procedure.

The drilling in 2002 a new cross section of observation boreholes which was located perpendicularly to groundwater flow in the distance of 1.2 km from the Building 31 allowed a plume of mercury contaminated groundwater going from the main center of mercury pollution to the north-northwest direction to be disclosed. Contouring this plume showed that it is maximum 350 m broad and more than 2 km long, at that the flow of the polluted water moved over the layer of basalt clay of Pavlodar's suite at the depth from 6 down to 14 m depending on a relief and surface geometry of basalt clay layer (fig.8). The concentration of mercury within the plume changed from 65 µg/l (130 MPC_w) near the Building 31 to 50 µg/l (100 MPC_w) near the 6th wastewater pumping station and further up to 45 µg/l (90 MPC_w), 0.8 µg/l (1.6 MPC_w), 1.1 µg/l (2.2 MPC_w), 0.9 µg/l (1.8 MPC_w), 0.4 µg/l (0.8 MPC_w) every 200-300 m. Ten new observation boreholes that were drilled to the west from the plume of mercury contaminated groundwater showed that the distribution of mercury pollution to this direction is not revealed.

Fig.8. Hotspots of groundwater contamination with mercury above 500 ng/l according to 2002 investigation of observation boreholes

Surface water in the special ponds being accumulated because of atmospheric precipitation was contaminated with mercury up to a level of 50 mg/l (100000 MPC_w), in pits to the south from the special ponds - from 3 to 30 µg/l (6-60 MPC_w), in the drain going along the motorway in the direction to western dam of the pond Balkyldak - from 2 to 18 µg/l (4-36 MPC_w), in the pond Balkyldak near the special ponds - from 3.5 µg/l (7 MPC_w) up to 100-300 ng/l (0.2-0.6 MPC_w) in shoaling water along the rest of the coast. The mercury contents in water of an unfinished emergency canal extended from the pond Balkyldak to the Irtysh River was not more than 10 ng/l (0.02 MPC_w), in floodplain lakes of the Irtysh River near the villages Pavlodarskoe and Shauke - not more than 9 ng/l (0.018 MPC_w), in the Irtysh River - was lower than the detection limit 2 ng/l (0.004 MPC_w) of used analytical procedure.

The mercury concentration in the sludge of the special ponds ranged from 10 mg/kg to 10000 mg/kg (2-2000 MPC_s), in bottom sediment of the pond Balkyldak – from 1 mg/kg to 500 mg/kg (0.5-250 MPCs). Groundwater moving from the special ponds to the pond Balkyldak on the depth of 1.5-2 m was contaminated with mercury up to the level of 2-3 mg/l (4000-6000 MPC_w).

Silver crucian is the main fish species living in the pond Balkyldak. Predatory fishes were not found there. Total mercury concentration in tissue of fishes caught from the pond Balkyldak ranged from 0.18 up to 2.2 mg/kg and exceeded MPC_f for non-predatory fishes (0.3 mg/kg) in most cases. Concentration of mercury in tissue of predatory fishes (mainly pike) caught in the Irtysh River and its floodplain lakes near villages Pavlodarskoe and Shauke, ranged from 0.075 to 0.16 mg/l that did not exceed 0.3 MPC_f for predatory fishes (0.6 mg/kg).

Gramma grass taken near the 6th wastewater pumping station contained mercury from 1 mg/kg to 2 mg/kg, however, mercury contents in milk, kidneys and liver of cows pastured in the territory between the Industrial Site #1 and the pond Balkyldak did not exceed a similar parameter for these products from other not polluted areas. Two samples of a hair belonged to employees of PCP contained mercury at the same level as a hair of residents of Almaty.

2.2 Risk assessment and recommendations on remediation

Scares studies of 1989-1993 did not allow overall estimate of risks coming from the mercury pollution within PCP. Demercurization Design of JV Evrohim /28/ was based on assumption that huge amount of metallic mercury (about 1000 t) deposited in concrete floor of the Building 31 and in soil underneath the building posed principal threat to environment. That time high market value of metallic mercury gave hope that its recovery would ensure covering most costs to dismantle equipment and the Building 31 became worthless. All the rest infrastructure of chlorine production was supposed to keep intact and to use in the future in chlorine production based on membrane method /29/.

In process of dismantling of equipment and electrolysis hall of the Building 31 in start period of demercurization works in 1998-1999 about 140 tons of metallic mercury were collected including 20 tons of spilled metallic mercury manually from the floor of the building. Some part of collected metallic mercury was spilled again during transportation of the equipment and building structures outside the Building 31 and formed huge hotspots of topsoil mercury contamination within the industrial area of PCP, which were released during investigation of 2000-2002. After dismantling of the roof and walls concrete foundation of the Building 31heated up in the sun and metallic mercury "sweated out" on its surface forming mercury puddles. All this resulted in uncontrolled emissions of mercury to atmosphere maximum of which fell on time of the Building 31 dismantling works (up to 100000 ng/m^3), but still significant during break in the clean up works in 2000-2002 (up to 25000 ng/m^3) and hitherto persisting (up to 17000 ng/m^3) despite construction of a few clay screens containing concrete foundations dismantled buildings of the chlorine production including the Building 31.

Groundwater mercury contamination did not pose any perceptible risk in spite of its 2.5 km spread from the Building 31 because of its occurrence at the depth of not less than 5 m in desert places (5 km far from the Irtysh River and 4 km far from nearest settlement). To estimate the potential risks computer simulation was carried out which showed (the first variant of prognosis) that the plume of groundwater polluted with mercury would spread to the north-northwest direction at the depth from 5 m to 15 m over the clay layer of the Pavlodar suite (fig.9). If the direction of groundwater movement does not change, there will be no serious threat to inhabitants of Pavlodarskoe village and Irtysh River. However there it will be possibility for a small amount of mercury to get into the emergency discharge canal whose construction is not finished yet going from the pond Balkyldak to the western direction. The third variant of the prognosis (fig.10) showed that the direction of spread of mercury contaminated groundwater plume can change if hydro-geological conditions are different. Cessation of water losses from underground water supply system using to provide enterprises of the Northern industrial area of Pavlodar with water can affect a configuration of groundwater surface and the direction of their movement. As a result the plume can change its direction to the west and threat to Pavlodarskoe village and Irtysh River can arisen. The second variant of the prognosis allowed the conclusion to be done that construction of an anti-filtration screen so called "cut-off wall" around the source of mercury under the Building 31 would not solve completely the problem of improvement of groundwater quality, as one more source of pollution less strong though still remained in the area of the 6th wastewater pumping station. The fourth variant of the prognosis (fig.11) showed that without these two sources of contamination the plume in 2005 must split into two areas. At that by 2031 the south area will decrease to 100 m in diameter and its center will be located 100 m eastward from the 6th pumping station and mercury concentration in it will decrease to 2-6 MPC_w. The north area will have a center located 0.5 km westward of special ponds, its maximal spread will not increase 0.85 km, and mercury concentration in groundwater will not reach the value above 15-20 MPC_w. Thus at isolation of the both sources of mercury entering to groundwater potential risk posed by groundwater mercury contamination can be minimized.

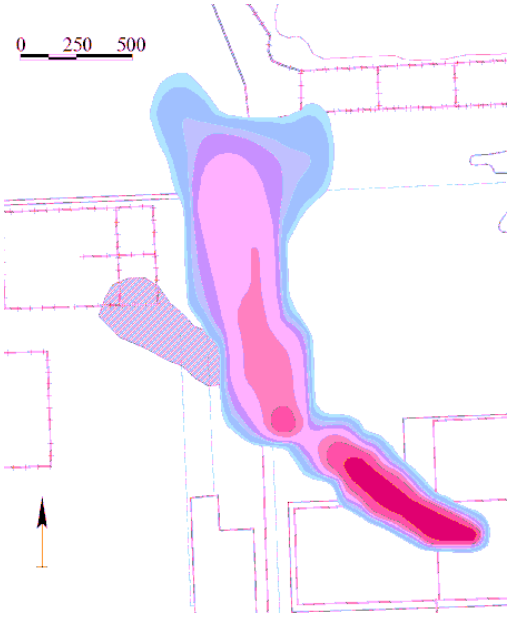

Fig.9. Spread (m) of plume of groundwater mercury contamination on the results of simulation of hydro-geological conditions as of 2031 (first prognosis scenario)

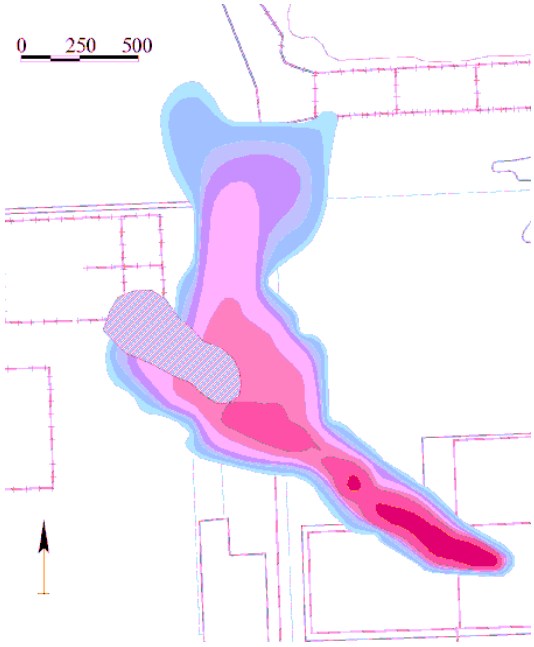

Fig.10. Spread (m) of plume of groundwater mercury contamination on the results of simulation of hydro-geological conditions as of 2031 (third prognosis scenario)

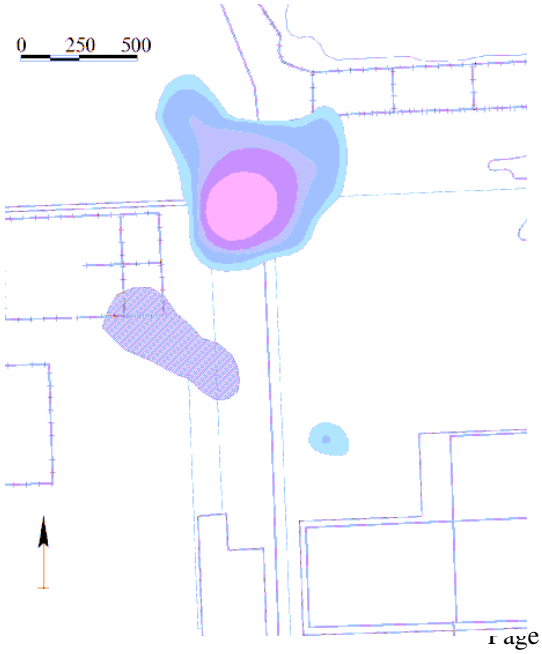

Fig.11. Spread (m) of plume of groundwater mercury contamination on the results of simulation of hydro-geological conditions as of 2031 (fourth prognosis scenario)

Conclusions on risk assessment and recommendations on remediation made as a result of implementation of INCO-2 ICA2-CT-2000-10029 "Toxicmanagement" project:

Mercury contamination of groundwater used for drinking water supply. In northern and northwest suburbs of Pavlodar City all boreholes used for drinking water supply contain mercury of lower concentration than permissible level. This territory includes Pavlodarskoe village. Water supply using groundwater in this area can be considered as safe from mercury contamination.

Mercury concentration in water and fish of the Irtysh River and its floodplain lakes. There is no any considerable mercury contamination in the Irtysh River and fish inhabiting it; the mercury concentration there is much lower than the maximum permissible concentration.

Mercury contamination levels in the area of the former electrolysis shop. It is necessary to finish the works projected by JV Evrohim as soon as possible and connected to encapsulation of the main hearth of the contamination from an environment. The building 31 should be demolished and its building structures placed into a landfill. Also construction of the bentonite cut-off wall reaching down to regional basalt clay layer should be completed. If the cut-off wall functions in accordance with the plan and prevents the groundwater containing soluble salts of mercury from further horizontal spreading there is no necessity to take out and clean the concrete floor slab of the electrolysis hall of the shop 31, and also ground under it. The thermal treatment of the construction materials, strongly contaminated with mercury can be postponed for the future, when mercury price probably increase and its extraction becomes economically justified. However in this case it will be necessary to isolate things confined by the cut-off wall, so that it will become impenetrable for atmospheric precipitation from outside and mercury vapor from inside that will stop polluting an atmosphere. It will require construction of specially designed cap (which also should stop capillary lifting) further to the works which were designed by JV Evrohim's design.

Mercury contamination of soil around chlorine and caustic soda production. The soil contaminated above sanitary norms which is outside the territory confined by cut-off wall, should be taken out and placed into specially designed landfill and isolated from action of groundwater and atmospheric water.

Mercury pollution of ambient air. Under demercurization work carrying out it is necessary to take dust-depressive measures, to use more efficient temporary covering for mercury contaminated soil and the concrete floor slab of the hall of the shop 31, and also to stop using the existing plant for thermal treatment of mercury containing construction materials (fig.12).

Spread of the mercury contaminated groundwater plume. The plume of mercury contaminated groundwater does not threaten the Irtysh River and Pavlodarskoe village if there is no considerable additional interference changing adversely hydro-geological conditions in the Northern industrial site in Pavlodar. If the original source of mercury contamination which occurs under the Bbuilding 31 is contained, then even under adverse changes of hydro-geological conditions the mercury will not be able to reach the Irtysh River and Pavlodarskoe village. Demercurization conducted in addition to work stipulated by JV Evrohim demercurization project and also the containment of the secondary source of contamination - 6th wastewater pumping station with the help of the cut-off wall will stop the further local mercury contamination of groundwater.

Special evaporation ponds for liquid and solid mercury wastes. In addition to work stipulated by JV Evrohim demercurization project it is necessary to isolate the special ponds for

mercury wastes with the help of bentonite cut-off wall reaching the regional basalt clay, and specially designed cap, impenetrable for mercury vapor and atmospheric water.

Wastewater storage pond Balkyldak. FISH FROM WASTEWATER STORAGE POND BALKYLDAK CONTAINS TOXIC LEVELS OF MERCURY. FISHING FROM THE POND SHOULD BE PROHIBITED IMMEDIATELY AND THE ACTIVE STEPS FOR IMPOSING THIS BAN SHOULD BE UNDERTAKEN. It is necessary to continue studying the wastewater storage pond Balkyldak status in order to make long-term decision associated with its mercury contamination.

Fig.12. Plant for thermal demercurization of solid waste

2.3 Gaps of knowledge

The research of 1989-2002 revealed the ways of mercury spread on food chains and degree of its effect on population health living in this region (except for founding high contents of mercury in fish of wastewater storage pond Balkyldak which is a place of both private and commercial fishing). Potential risks posed by the pond Balkyldak were assessed only approximately because the problems of this huge water body (including at the cost of mercury deposited in its bottom sediments) were investigated insufficiently and mainly on historical data.

Works on mercury contamination clean-up conducted in 2002-2005: buildings dismantling and utilization of production equipment, containment of under ground mercury hotspots, and construction of landfill for mercury contaminated building materials have changed significantly the situation in the area of pollution including due to transport of big amount of mercury contaminated materials.

In September 2004 AIPET and PCP undertook a joint field and chemical-analytical studies to determine mercury concentration at the final stage of demercurization works. The research was funded via EU 6FP "BIOMERCURY" project and from resources of PCP /30/. 36 new monitoring boreholes were investigated which were drilled in autumn 2003 as well as 49 old boreholes designated for investigation by the Program of demercurization. 6 samples of surface water, 11 samples of soil, 15 samples of air, and 4 samples of fish from wastewater storage pond Balkyldak were taken.

Comparison of the data of 2004 and one received on "Toxicmanagement" project in 2001-2002 showed that as a result of man-caused intervention in hydro-geological conditions at the area of mercury hotspots in 2003-2004 some local changes in mercury concentration in groundwater within the contamination plume have happened.

In some cases when a borehole happened to locate in the site surrounded by a cut-off wall concentration of mercury could go up drastically, for example 100 times increase in mercury concentration was found for the borehole P3. The same happened for the boreholes located in the site of ruined sewage communications, for example 10 times increase in mercury concentration was found for the borehole 87-02, and double one - for borehole B21a. At the same time the boreholes located in the immediate vicinity to cut-off wall showed decrease in mercury concentration there, for example, double decrease in mercury concentration was found for the boreholes 566-00 and 567-00. For the most boreholes located quite far from the area of demercurization works the change in concentration level in groundwater did not happen. Study of new boreholes drilled in 2003 proved the high level of mercury concentration in groundwater within earlier found hotspots, especially near the special evaporation ponds. Besides one more hotspot was found in the site of former mercury sewage system connecting the industrial site #1 and the special evaporation ponds.

Levels of mercury concentration in the surface water in the area of demercurization works increased significantly, including ones in shoaling water along south-west shore of the wastewater storage pond Balkyldak. It came from the relocation of great volumes of dust-forming mercury contaminated soil.

Levels of mercury concentration in soils in the area of demercurization works remained considerably high, which probably was accounted for non-completed activity at the moment of sampling. The same places where soils were heavily contaminated by mercury were the main sources of mercury entering to atmosphere. Levels of soil mercury contamination outside the mercury hotspots (for example westward from Central Laboratory) remained insignificant.

It turned out that in September 2004 it was hard to estimate a long-term impact of the demercurization works on environment in the area of PCP due to the incompleteness of this works that time. One can notice local short-term increase in level of mercury danger in the area of the works caused by dust forming and mercury emissions from the experimental thermal plant for treatment of mercury containing construction waste. That increased risk for the workers involved in demercurization works.

Pavlodar Regional Territorial Environment Protection Department offered to develop Program of post-demercurization monitoring within the clean-up works, which they supposed to finance from Pavlodar oblast budget. The Program of mercury monitoring in the Northern industrial area of Pavlodar /30/ was developed by AIPET in 2004 in compliance with agreement between PCP and AIPET. Main necessity of its development was justified by the fact that the mercury contamination hotspots were isolated and not removed. In such conditions the mercury monitoring became the main means of information receiving for decisions making.

The main goals of Program of the mercury monitoring were (i) determination of levels of mercury content in various environmental objects (atmosphere, soil, surface water and groundwater) which remained after implementation of the Program of demercurization of chlor-alkali production at the former PO "Khimprom", (ii) control over these levels changes during 15-year period, and (iii) confirmation of acceptable level of risk posed from the residual mercury contamination for public health, including population of northern suburb of Pavlodar and people working on the territory of the former PO "Khimprom".

Field studies and computer simulation carried out in the framework of the "Toxicmanagement" project in 2001-2002 /26-27/ have shown that the major risks caused by mercury contamination in area of the former PO "Khimprom", Pavlodar were connected with mercury contamination of groundwater and surface water as well as with evaporation of mercury on sites of the most intense contamination of soils.

As a result of implementation of the Program of demercurization the risk caused by pollution of atmosphere by mercury should be considerably reduced. Entering of mercury to natural water will also be stopped that in turn will lead to their gradual self-cleaning and reduction of the risk related to the mercury contamination of groundwater and surface water. One should expect keeping the level of mercury contamination of soil in area of the former PO "Khimprom" however the area of this contamination is not expected to spread further. Therefore the monitoring of mercury contamination in the area of the former PO "Khimprom"should include the following components:

- control over exceeding of MPC_{gm} for gaseous mercury equal to 300 ng/m^3, in near-earth atmospheric layer (1 m) at the industrial site #1 of the former PO "Khimprom";

-control over exceeding of MPC_s for total Hg, equal to 2.1 mg/kg in the soil layer covering mercury landfills;

- control over absence of spread of mercury pollution in soils with Hg exceeding MPC_s for total Hg equal to 2.1 mg/kg outside of original mercury aureoles (including at the cost of evaporation of mercury contaminated groundwater) and control over absence of accumulation of mercury inside of original hotspots of the mercury contamination;

- control over absence of spread of groundwater with Hg concentration exceeding MPC_w for dissolved inorganic mercury equal to 500 ng/l toward Pavlodarskoye village and the Irtysh River;

- observation over decrease in total Hg concentration in groundwater, including the groundwater within the mercury pollution plume;

- control over absence penetration of Hg dissolved into groundwater outside of cut-off wall and landfills for solid mercury wastes; and observation over level of groundwater inside of the isolated volumes;

- observation over levels of total Hg concentration in surface water of the Northern industrial area of Pavlodar, including the wastewater storage pond Balkyldak;

- observation over levels of total Hg concentration in fish of wastewater storage pond Balkyldak.

To achieve these objectives the following tasks had to be solved:

- determine the order, periodicity and methods of air, soil and water sampling for their analysis for total mercury;

- determine the order and periodicity of other field activities and measurements;

- determine the methods of chemical analyses for total mercury in samples and order of laboratory works;
- develop recommendations on the obtained results interpretation;
- determine resources needed for the mercury monitoring.

The results of suggested Program of mercury monitoring should answer the question whether the demercurization activities of 2001-2004 at the area of the former "Khimprom" were sufficient. In case of decease in the residual mercury contamination to the level of acceptable risk the Program of mercury monitoring can be completed in 2020. In case of detection of increase in risk for the environment and public health due to increase in mercury concentrations in soil, surface water and groundwater as well as in case of detection of atmospheric contamination with gaseous mercury it will be necessary to consider the additional measures on clean-up of this territory from mercury or its engineered protection at any stage of the Program of mercury monitoring.

In 2005 Pavlodar Regional Territorial Environment Protection Department could allocate 5 million tenge from the oblast environmental fund for the first Phase of the Program of mercury monitoring. This is minimal sum required for such sort of works to be carried out by local up-to-date accredited chemical-analytical laboratory. However at present there is no such laboratory in Pavlodar. Laboratories remained since the soviet time have out-of-date worn out equipment and minimal staff which is predominately pensioners who can live on low salary due to having additional income. Establishment of up-to-date environmental monitoring laboratory requires investments. ISTC and the USA Government have an idea to create such laboratory in Pavlodar to engage scientists and engineers – former employees of PCP, who have expertise in chemical weapon production. These specialists pose a threat to the world community in case of their being unemployed.

AIPET, Pavlodar State University (PSU), IHH, SLM and PCP worked out a project proposal the purposes of which were:

- to identify the risk associated with the spread of groundwater plumes contaminated with mercury and oil derivates, including their movement through the network of water intake boreholes in village Pavlodarskoye, and further towards river Irtysh and/or their rise onto the pastures and, if significant, identify a management strategy to contain risk;
- to identify a management strategy for containing the environmental risk, caused by the mercury pollution of lake Balkyldak, including the pathway of pollutants bioaccumulation via food chains.

Project objectives:

- study of the movement of mercury in the groundwater rise in depressed area in saturated and unsaturated zones and its accumulation in the shallow ponds and vegetation. Development of management strategy to contain the risk to population in the vicinity and livestock;
- facilitation of the Laboratory of environmental protection of PCP with the equipment for conduction of mercury monitoring, and training of the local staff;
- carrying out 3-year post-containment monitoring program in the Northern industrial area of Pavlodar, including the monitoring of soils and vegetation of pastures in the close vicinity of contamination, and development of recommendations for the further implementation of the monitoring program;
- assessment of possibility for mercury-polluted groundwater flow to change its direction; study of interaction of contaminated groundwater with bearing strata and underlying aquifers;
- upgrading and detailing the models of groundwater in the Northern industrial area of Pavlodar and contamination of groundwater with mercury;
- investigation of the possible connection in the aureole of mercury pollution between the groundwater of Low-Medium Pliocene deposits of Pavlodar assise and groundwater of Oligocene deposits of Nekrassovskaya suite;

- definition of more accurately prognoses for spread of mercury-containing groundwater in Northern industrial area of Pavlodar taking into account adsorption/desorption of mercury on bearing strata of aquifers and on surface of basalt clay;
- study of the spread of groundwater plume contaminated with oil products from the territory of POR; development of model and assessment of environmental risk posed by oil-products contamination of groundwater in the Northern industrial area of Pavlodar;
- facilitation of the Laboratory of environmental protection of PCP with the equipment to monitor contamination of groundwater with oil products, and training of the local staff;
- drilling and equipping new observation boreholes for groundwater sampling and their chemical analyses in order to define the direction of spreading the plume of groundwater contaminated with oil and petroleum derivates;
- development of the model of spreading the oil products with groundwater in Northern industrial area of Pavlodar;
- assessment of possibility to contain the risk posed by mercury pollution of the pond Balkyldak including the fish within it;
- study of the mercury contamination of bottom sediments in the pond Balkyldak, and estimation of the amount of deposited mercury;
- study of the food chains of the pond Balkyldak and to assessment of the bioaccumulation of mercury in aqueous organisms;
- development and discussion with local stakeholders the recommendations for the second Phase of demercurization and other remediation activities in the Northern industrial area of Pavlodar in the area of PCP, including the recommendations for abolishment or further safe use of the wastewater storage pond Balkyldak.

One of the most important objectives of the works to be implemented was the creation of monitoring laboratory PCP capable to carry out the Program of post-demercurization monitoring in the Northern industrial area of Pavlodar in 2005–2020. This laboratory together with AIPET will carry out the first stage of monitoring studies of the mercury contamination. The monitoring of groundwater contamination with oil and oil derivates will be conducted by SLM in cooperation with PCP. PSU together with AIPET will carry out the study of mercury contamination of bottom sediments and biota from wastewater storage pond Balkyldak. AIPET together with IHH will make the risk assessment posed by residual mercury contamination on the territory of the former PO “Khimprom” and around it, as well as assessment of risk from groundwater contamination by oil products. IHH will also upgrade the groundwater model for the Northern industrial area of Pavlodar and make it more accurate. This will allow making proposals to manage the contamination of groundwater by mercury and oil derivates. Suggestions for risk management in Northern outskirts of Pavlodar will be drawn up and discussed with local stakeholders and state authorities. This will include possible implementation of the second Phase of the former PO “Khimprom” demercurization and/or brining wastewater storage pond Balkyldak to safe conditions.

Project proposal was discussed in ISTC in October 2004, approved by a collaborator and American partners, as well as by the Government of the Republic of Kazakhstan and received funding from US EPA since October 1, 2005 as ISTC K-1240p project.

3. Solutions - treatment options

3.1 Description of treatment methods

3.1.1 Demercurization Design of JV Evrohim /28, 31-34/

The development of the project was carried out in 1988–1995 and coincided with the USSR collapse and years of economical and political crisis. In this period huge Institute KNIIF GOS-NIICHLORPROEKT was reorganized into KNIF MNPO "Sintez", then into KNII "Sinteko", which in turn gave life to a small company JV Evrohim while PCP was brought to the verge of bankruptcy. However PCP funded the project development mainly from its budget.

Priority program of demercurization developed by JV Evrohim as a result of the study of 1988-1992 lay in the dismantling of the most contaminated parts of the Shop 31 - electrolyses hall (80 electrolyzers, other mercury bearing equipment, walls, floor slabs, etc…), washing the dismantled structures at the place and their sorting out. Metallic equipment after their treatment with oxidants (sodium hypo chloride, hydrogen peroxide, potassium permanganate, nitric acid, ferrous trichloride) and water and had to be utilized as a scrap metal, building structures with less then 1% of mercury – to be put in the specially constructed landfill (a pit of 3 m deep bottom of which was lined with clay screen of 0.5 m thick and with potential to be increased) and filled up with liquid cement. The building structures of more then 1% of mercury content had to be temporarily stored in the area of 1500 m^2 and covered with clay. The most contaminated materials had to be collected in containers and to wait for their treatment. Other less contaminated parts of the Shop 31 were supposed to be dismantled later.

Main process of mercury recovery was expected to be carried out with the use of plants of thermal demercurization of concrete and mechanical demercurization of ground. At that concrete and ground after recovery of the most amount of mercury from them also had to be placed to the new sections of the landfill and filled up with ground-concrete mixture.

Concrete debris from the floor of the electrolysis hall of 20x30 cm size with mercury concentration of 0.3-0.5% had to be treated in the vacuum chamber electrical furnace of periodic operation under 700-750^oC temperature for 2 hours. It was planned to cool the air containing mercury vapor in an air condenser with additional water cooling. Metallic mercury had to be periodically poured into hermetically sealed containers while the cooled air to undergo additional treatment with adsorbent HPR-3p (activated charcoal soaked with ferrous trichloride), and then to be emitted in the air through 10 m high chimney.

Grounds with mercury concentration more then 1% had to be cleaned from mercury by preparing the pulp and its screening at the scrubber equipped with a trommel. The pulp poor with mercury which was obtained as a result of this operation was partly dehydrated and sent for ground-concrete mixture preparation and filling up the landfill with help of a pump.

Grounds with concentration less 0.3% (close to Shop 31) and less 0.02% (close to Shops 31a and 37) had to be excavated from the depth down to 0.25 m and used for ground-concrete mixture preparation with no preliminary treatment.

Ground-concrete consisted of (per 1 m^3 mixture): ground – 1800 kg, Portland cement (H 400) – 95 kg, water – 300 kg (totally 2195 kg). Design toughness of concrete – 1.5 MPa. Prepared ground- concrete mixture had to be brought to the landfill with help of tracks.

The landfill for mercury wastes had to consist of sections (not less then 3 ones) and to have capacity up to 33300 m^3. The landfill should be covered with clay and asphalt screens from the top on which industrial facilities could be located in the future.

Suggested rate of mercury recovery: at ignition – 95, at screening - 85%, maximal mercury concentration in the buried concrete – less 3.5%.

In 1996 JV Evrohim's design was supplemented with Feasibility Study on dismantling and demercurization of the Electrolysis Shop.

3.1.2. Proposal of Japan Consulting Institute /29/

During his visit to Japan in 1993 the President N. Nazarbayev had negotiation with Japan Government on participation of Japanese companies in elimination of mercury contamination in Pavlodar and construction of new chlor-alkali production based on membrane method. On the instruction of Japanese government Consulting Institute gave consultancy for JV Evrohim and conducted their own study of the problem. The tasks of the study were as follows:

- elaboration of recommendations for appropriate technology of caustic soda and chlorine production;
- study of the stopped production with respect to maximal use of existing facilities and minimal investment of additional funds;
- caustic soda, chlorine and hydrochloric acid market research to determine the adequate capacity of the plant;
- development of recommendations for more efficient project implementation;
- financial and economic analyses of the project implementation and providing results of the estimation.

The plan of the production conversion was developed based on both replacement of electrolysis technology of chlorine and caustic soda production by membrane one and allocation of new membrane electrolysis units together with the most part of old equipment in new building. The plan of works proposed by JV Evrohim was accepted as a basic plan of demercurisation. It was expected that the funding for demercurization activity would come from the soft loan provided by the Japanese Government. For this deal PCP had to get the guarantees of Government if the Republic of Kazakhstan, however such guarantees have never been received. Thus the negotiation came to an end with no success.

3.1.3. Participation of BRGM Company (France)

In 1999 the Minister of Mineral Resources and Environmental Protection of the Republic of Kazakhstan visited France. During his visit he held the meeting with French companies interested in demercurization activity in Pavlodar. These activities lay in the provision of soft loan from French government, technical support and participation of French firms and technologies in the project implementation. BRGM – is a French national company dealing with ore deposits mining and wastes disposal - started cooperation with Ministry of National Resources and Environmental Protection of the Republic of Kazakhstan (MNREP RK) and PCP in elimination of the mercury pollution. As a result of the first mission of BRGM "Contamination spread prevention program" was submitted to the Minister S. Daukeev, which was approved on August 3, 1999. /35/.

In compliance with the original proposals of BRGM remediation of the mercury contamination in Pavlodar was supposed to consist of four phases. Phase "A" lying in 10-day mission of French experts implied familiarization with the problem, technical aspects discussing and data collection. Along with it the proposal for World Bank to fund the Phase "B" had to be prepared. Phase "B" lay in assistance in burial of mercury containing wastes of PCP (i.e. in fact in conducting initial stage of JV Evrohim design). Indicative budget of this Phase amounted $2 million, $0.4 million of which had to be covered by French party and $1.6 millions – by Kazakhstan party (or through a World Bank loan). Phase "C" consisted in remediation of contaminated area in the north suburb of Pavlodar to an acceptable level according to the project which had to be

elaborated by BRGM during the Phase "B". Indicative budget was $4 millions and had to be covered with the soft loan of French Government. Phase "D" had to provide for absolute safety of Pavlodar region from the mercury contamination at the cost of World Bank loan.

Next variant, "Demercurization project in Pavlodar: Environmental Impact Assessment and contamination hot spots elimination" was proposed by BRGM six months later /36/ and had three phases: Phase I – works on ensuring safety of concrete floor in Shop 31 (with durability of 2 months and cost of $0.3 millions of French Government soft loan); Phase II (consisted of two parallel components at the expense of French Government soft loan): component A – assessment of the pollution scale and health risk for population in Pavlodar (duration –18 months, estimate budget - $4 millions), component B – demercurization of 1500 m^3 of wastes with high mercury concentration on mobile thermal plant (duration - 18-24 months, estimate budget - $4 millions); Phase III – had to ensure integrated control over the situation and had to be determined on the base of Phases I and II results. During the visit of President of the Republic of Kazakhstan N. Nazarbaev to France in June 2000 these proposals were approved and in September 2000 a protocol on soft loan (€8.2 millions) to be provided by the French Government was signed. According to that protocol the yearly interest rate amounted 2.1% for 16 years period including 6 years on preferential terms and the next ten years the pay-outs had to be paid off by 20 equal parts /37/.

Nevertheless the protocol stipulated denial of JV Evrohim design as in compliance with the loan terms "…local expenses, services and equipment made not in France, should not exceed 10% of the whole loan…"/38/. Accordingly BRGM offered to MNREP RK to review the JV Evrohim design (including cancellation of landfill construction for materials with mercury concentration less than 0.3%, cut-off wall construction and mercury washing out of heavily contaminated grounds as well) and to divide the demercurization activities into three stages:

i – dismantle chlor-alkali facility, wastes sorting and burial in the temporary storage,

ii – reduce mercury concentration in grounds and soils to the maximum permissible level through their thermal treatment,

iii – ensuring the full safety of Pavlodar region from the mercury pollution.

PCP administration as well as the local authorities didn't accept the proposal to abandon JV Evrohim design completely. It was suggested that BRGM should develop Feasibility Study (FS) of their proposal /39/ for its further consideration as an alternative project to JV Evrohim's one. BRGM developed the project FS "Demercurization and elimination of mercury source of contamination in Pavlodar" /40/ and submitted it to MNREP RK at the end of December, 2000.

FS suggested conducting:

- collection of additional data on soil-ground characteristics at the Site #1 and on bottom sediments in the special evaporation ponds and the pond Balkyldak;
- assessment of water quality in the river Irtysh, groundwater and air quality;
- simulation of mercury migration with both groundwater and surface water as well as with the air which should be done to assess the risk posed to population;
- technical and economic assessment of efficiency of different technologies of cleaning from mercury;
- technical solutions developments on the site rehabilitation to be funded by World Bank;
- temporary encapsulation of concrete floor of Building 31;
- thermal treatment of 1500 m^3 most contaminated materials in a vacuum furnace;
- construction of anti-filtration screen – cut-off wall around Building 31.

FS also suggested approximate distribution of the loan funds (8.2 million Euros) as follow:

- technology and equipment purchase and personnel training - 50%,
- data collection and analyses, risk assessment - 25%,
- demercurization, rehabilitation works at industrial site and construction of cut-off wall - 25% .

After the comparison of JV Evrohim and BRGM proposals /40/ by Kazakhstan party it was evident that BRGM technology does not drastically differ from JV Evrohim proposal however

the cost of BRGM project was much higher then that of JV Evrohim. For example, the method of mercury recovery according to BRGM 20 times more expensive than that of JV Evrohim. In compliance with the BRGM proposal Kazakhstan had to get confirmation of already proven mercury thread and risks, conservation of the situation and recommendation for its liquidation for 8.2 millions Euros. Complete demercurization by BRGM was estimated as high as $ 80-130 million, while JV Evrohim design suggested the elimination of the source of mercury contamination for $ 6.5 million. It was recognized that "…BRGM project is a research one and does not solve the tasks of elimination of the source of mercury contamination put by the President and Government of the Republic of Kazakhstan, what was recognized by the authors of the FS…" /41/.

Comparison of JV Evrohim and BRGM designs gave reasons to Kazakhstan to insist on urgent implementation of JV Evrohim design at the expense of French Government loan with no any changes which would cause the delay in elimination of emergency situation. The negotiation lasted until the end of 2001 with no results.

3.1.4 Correction of JV Evrohim design /42,43/

Correction of the working design of demercurization developed by JV Evrohim in 1995 was recommended by National Academy of Science of the Republic of Kazakhstan (the letter of Vise President of NAS RK #481 of 13.05.2003) /44-45/. Necessity of such correction was caused by the fact that scope of work specified by the project and accomplished in 1998-1999 prevented substantially the tread of the Irtysh River mercury contamination from the Northern industrial area of Pavlodar. Besides in 2001-2002 the data on sufficiency of cut-off wall to encapsulate the mercury source was received and there were no need to extract and treat concrete floor slab and the soil from under the Shop 31. Moreover new hotspots of soil, groundwater and ambient air mercury contamination were found which required additional demercurization activities. It was also found that the special ponds for liquid and solid mercury wastes were very dangerous source of an environment contamination by mercury and need to be isolated from groundwater and ambient air urgently but not after completing first stage of demercurization works as it was scheduled in the project of 1995. At the same time it was ascertained that for the period of time passed since 1993 the buildings of the chlorine and caustic soda production had come to state of nonoperability and become the source of environment pollution by mercury and could not be used in productions newly being created. That brought to necessity to dismantle the building structures and equipment of the shops with their following demercurization.

Taking into account the technical characteristics of demercurization objects, their location in the industrial site and accumulated experience in demercurization activities the next methods of demercurization were suggested by the correction of the working design:

- confinement of both hotspots of groundwater mercury contamination and special evaporation ponds for mercury wastes with help of cut-off walls,
- excavation of topsoil heavily contaminated with mercury down to the depth of 0.5 m at some spots followed by their burial at the special ponds' sections. The area after excavation should be resoiled with clean ground,
- construction of a cap impermeable for mercury vapors and atmosphere precipitation on the top of areas confined by the cut-off walls including special evaporation ponds,
- demercurization of buildings and production structures through their dismantling, cleaning from sludge and debris followed by burial of the mercury containing wastes in the special ponds,
- creation of network of observation boreholes and acquisition of equipment for mercury monitoring to be done.

These technical decisions were amendments to the scheme of the whole demercurization project. They were chosen on the base of experience accumulated at PCP during the demercurization and lay in following:

- isolation of hotspots of mercury contamination and the special evaporation ponds from groundwater impact was carried out by constructing cut-off walls made of bentonite clays which reached the basalt clay,
- surface screening on contamination sites was carried out with piling and compacting bentonite types local clays on the top of the layer of clean soil,
- burial of demercurization wastes and debris was planned to do at the evaporation ponds with following the ponds isolation,
- isolation of filled special evaporation ponds from atmosphere was carried out by creating multi-layer cap: (i) intermediate leveling layer was consisted of materials from dismantled dams' crests, (ii) sorption layer was consisted of ash from the power plant and served for prevention of capillary rise of water and substances dissolved in it, (iii) waterproof layer was consisted of bentonite types clay, (iv) and protection of the cap against rainfalls was provided by the layer of fertile land with vegetation,
- asphalt top covering on the landfill for mercury wastes filled up with clay-concrete mixture was designed for dusting prevention,
- made decision on demercurization and construction of caps and coverings allow using these areas in future for constructions on their surface light buildings and structures without foundations and underground communications network.

3.2 Treatability studies of bioremediation technology

Since metallic mercury is predominant mercury speciation in contaminated soils in Pavlodar that potential to use biotechnology for their remediation is restricted very much. Speciation of mercury in bottom sediments of the wastewater storage pond Balkyldak have not been studied completely, however, one can assume that it must be mainly sparingly soluble mercury oxides deposited there. In principle there is possibility to transform these compounds from oxide form to sulfide one using sulfate reducing bacteria (this process goes with low speed in the nature), however literature data suggest that this does not lead to significant decrease in bioavailability of mercury in bottom sediments of bid freshwater water bodies.

Surface water of the pond Balkyldak is from time to time polluted with mercury when strong waving; when calm mercury concentration in the water goes down to 0.1 μg/L. It is evidence that suspended solids of sparingly soluble mercury compounds deposited in the bottom sediments are the main pollutant in surface water of the Balkyldak.

Biotechnology can be used for cleaning from dissolved mercury form mainly mercury chloride occurring in groundwater. However there are two problems making difficult using such simple solutions as, for example, pumping of contaminated groundwater and their treatment at the ground surface. The fist problem lies in the fact that presents mercury concentrations in groundwater (maximum of 200 μg/L) are lower of biotechnology capability, which use aerobic bacteria. The second problem is that most mercury distributed with groundwater at present must be adsorbed by enclosing rocks. From historical data in 1975-1993 during operation of chlor-alkali production mercury concentration in groundwater was much higher (tens even hundreds of mg/L), than at present time, that could be possible if losses of process solutions containing such strong oxidant as elemental chlorine filtered through grounds under the Building 31 contaminated with elemental mercury. In this case one should expect that amount of mercury fixed by enclosing rocks (clay predominantly) must be quite significant (tens tons) and observed present-day mercury concentrations in the plume of mercury contamination is a result of equilibrium of sorption – desorption processes. In such case replacement of polluted groundwater by clean one

would have no result because their repeated mercury contamination would happen quickly due to desorption processes.

At present Institute of Microbiology and Virology of Ministry of Education and Science, RK, Almaty (IMV) is developing biotechnology of immobilization of mercury both dissolved in water and adsorbed (but still reactive) by enclosing rocks using anaerobic bacteria resistant to toxic action of mercury (K-756p and K-1477 ISTC projects). The main problem arisen when developing this biotechnology is danger of mercury biomethylation. Absence of reliable data about conditions of this by-process behavior does not enable to say so far about considerable progress in these studies.

4. Pilot operation or final remediation

4.1. Experience of demercurization of chemical industries in the USSR in 1980s /46/

In 1981 the chlor-alkali production at JV "Khimprom", Sumgait, the Republic of Azerbaidzhan (currently it is surface-active material manufacturing plant) was shut down for reconstruction. Production shop was equipped with mercury electrolyzers CDM 50 with total capacity of 80 thousand tons of caustic soda per year. The production has been under operation for 25 years. A new electrolysis building was constructed 15 m far from the old one. Although it was equipped with the more advanced mercury electrolyzers CDM 100 its capacity was the same. It allowed the old chlor-alkali infrastructure to be kept.

There was no any special demercurization activity there. Mercury was poured out electrolyzers and other equipment and utilized in new production. Demercurization of the equipment was conducted by mechanical treatment of metal constructions and their rinsing with water followed by their sending to metallurgical works for remelting. Concrete building structures of the electrolysis factory were dismantled for a year and used by population in private construction. Sludge and debris rich in mercury was sent to Nikitovskiy Mercury Combine in Ukraine while wastes poor in mercury were sent to a landfill. For some time the floor of electrolysis factory was in the open air and mercury "sweated" out of the concrete. It was periodically mechanically collected. Later the floor was crashed and together with ground dug down to the depth of 2 m buried at the landfill. At present at the site of the old electrolyses factory there is a foundation pit where concrete columns of the building foundation were left.

In 1987-88 the old chlor-alkali production was closed down at PO "Kaustik", Sterlitamak, Russia. Its productive capacity amounted 80 thousand tons of caustic soda per year. New chlor-alkali production with mercury cathode was of double capacity and was constructed 5-6 years before the old production shutdown. It was located significantly far from the old one. JV "Evrohim", Kiev (JV Evrohim) developed the project of facility dismantling and demercurization of production buildings. Employees of the closed factory participated in demercurization activity which lasted a year. Not only equipment of electrolysis factory but also all ancillary technological facility of chlor-alkali production were dismantled and utilized. Besides mercury poured off the electrolyzers additionally about 140 tons of mercury was collected. Mercury sludge, debris and crashed floor of electrolysis shop were sent to Nikitovka Mercury Combine in Ukraine. Ground was not excavated as the building of electrolysis factory was constructed on the thick clay lens. Structures of large dimensions were buried in the landfill of I class hazard. Buildings of chlor-alkali production were kept as they were, including the electrolyses factory.

Dismantling of equipment of the old chlor-alkali production took place under the pressure of local mass media and NGOs requiring precaution measures to be taken because PO "Kaustik" is located within the residential area.

4.2 Demercurization of chlor-alkali production in Pavlodar in 1998-1999

Due to environmental emergency situation at PCP the head of oblast administration D. Akhmetov immediately after approving JV Evrohim design by MNREP in 1995 asked for The Republican authority to fund the demercurization activity. It was expected that the funding in 1996 would be provided by the Environmental Fund and national budget but the Ministry of Finance reject the funding due to the budget deficit (Letter to the RK Government of 07.03.96 №18-2-3/1644) and suggested using the debt capital from foreign investors and other stake-holders interested in production of caustic soda by non mercury method. Committee on Emergency showed no support to The head of Pavlodar administration either and the problem of funding was

deferred until 1998. However PCP used its own budget 18.53 million tenge and 6.7 million tenge of oblast Environmental Fund for certain works such as JV Evrohim design expertise, partial dismantle of Building 31, etc.) /47/.

Decision to allocate funds from the National budget (246 millions tenge in 1998, 373,4189 million tenge in 1999, 262,8295 million tenge in 2000, total: 882,2464 million tenge) /47/ was managed to receive only after the project of demercurization was separated from the project of construction of new production (Protocol of meeting at Deputy Prime-Minister № 20-11/9195 of 15.08.1997) /48/. A considerable pressure to take the decision to open the funding for demercurization activity was rendered by the Russian Federation Government: in 1998 in Moscow the RK Ambassador discussed with the RF Government the thread of mercury contamination of the transboundary Irtysh River, and on 10.04.98 the Protocol on Agreement between Pavlodar and Omsk administrations related to the measures to be taken to localize and eliminate the mercury hot spots /48/ was signed. In 1998 five years later after the production stoppage dismantling of Building 31 (Fig.13-14) and wastes burial was started. These works were funded from local budget because the national budget could provide 9.3 million tenge for the first year /47/. Dismantling of electrolyses shop was scheduled for winter 1998-1999 because mechanical collection of mercury is safer under the cold temperature (mercury vapor concentration inside the Building 31 in August 1998 was measured as high as 1.03-1.68 mg/m^3, i.e. more then 100 $MPC_{w.a.}$ /49/). In November 1998 3993 kg of mercury was manually collected /50/ and in December the dismantling of roof, carcass, walls and floor slabs (Fig.15-16) and the disassembling of the production equipment in the Shop # 31 were started.

Fig.13. Building 31 – electrolysis shop (northern side) before demolishing the building, winter 1998/99.

Fig.14. Building 31 – electrolysis shop (southern side) before demolishing the building, winter 1998/99.

Fig.15. Building 31 – electrolysis shop (northern side) after dismantling the roof, winter 1998/99.

Fig.16. Building 31 – electrolysis shop (northern side) after dismantling the roof, winter 1998/99.

At that during the dismantling more than 15 tons mercury was spilt /51/. Since the budget funding in 1999 was not opened yet, the works were carried out very slowly and finally also came to a stop. It worried a lot local environmental NGOs which for example held a picket of RK Parliament on 03.03.99 to attract the attention to the Mercury problem in Pavlodar. With spring come the intensive mercury vapors emission from the floors of the electrolysis hall started. By the decision of Pavlodar mayor, N. Chmykh №17 dated 02.04.1999 the territory of PCP was declared as a zone of emergency since 05.04 through 30.05. It drew the attention of public and mass media as well as national TV channels. The works on demercurization were intensified however the funding allocated for the emergency situation elimination was enough only for the mercury collection (17 ton /52/), dismantling and decontamination of equipment (electrolysers and metal constructions with obvious mercury contamination were washed up with high pressure water shower and then buried in the landfill /53/, 72 amalgam decomposers together with remaining mercury and graphite were transported to the cell #1 of special evaporation ponds for their temporary storage /53, 54/ but in fact were buried there /55/), dismantling and demercurization of the electrolysis hall of the Shop #1 and construction of the first section of the landfill. In late 1999 RK Prime Minister K.K. Tokayev visited Pavlodar oblast and after his visit the Plan of decontamination measures for PCP was developed and approved according to which in 2000-2002 the funding of $12.0 million had to be provided including $9.2 million from external loan and $2.8 million from the National budget /56/. However the money received in 2000-2001 were enough only to support the infrastructure of PCP (Table 1). New stage of funding for the demercurization was provided only in 2002.

Table 1. Cost of demercurization works at chlor-alkali production in Pavlodar in 1996-2001 (established prices) /57/

Funding sources	1996	1997	1998	1999	2000	2001	Total
National budget	-	2.0	9.3	80.0	30.0	-	121.3
Oblast budget	0.4	0.6	26.5	10.7	13.3	16.5	68.0
Own PCP funds	17.3	5.0	4.4	6.9	-	-	33.6
Total in the year:	17.7	7.6	40.2	97.6	43.3	16.5	222.9

4.3 Completion of first phase of chlor-alkali production demercurization program in Pavlodar in 2002 – 2004 /58/

In 2002-2004 after correction of JV Evrohim's design following works were conducted: Dismantling of Building 31 was completed as well as Buildings 34, 34a, 34b (only concrete floors of these shops were kept) and tanks of Shop # 34b and 6th pumping station; Buildings 37, 36, 36b, 31d, 109 and water recycling communications were decontaminated; infrastructure objects including overpasses and rail and auto ways were either carried to different places or dismantled; cut-off wall 0.6 m wide and 9-20 m deep made of benthonic clay was constructed around four main hotspots of mercury contamination so that it was 1 m deepened into the basalt clay. Cut off wall was being dug with special excavators (fig. 17-19) by digging the trench under the protection of bentonite solution followed by its filling with clods of bentonite type's clay. Its total length is 3588 m, including around the Building # 31 – 699 m (19-20 m deep), around shops 31a, 34 and 40 - 185 m (19-20 m deep), around 6th pumping station – 240 m (11-12 m deep), around the special evaporation ponds for mercury wastes – 2464 m (9-12 m deep). Soil contaminated only from the surface was excavated down to the depth to 0.4 m and removed in the special evaporation ponds to be buried. Instead the removed topsoil bentonite type's clay layer 0.2-0.4 m thick was put there (fig. 20), which produced the clay screen with area of 31180 m^2. Special evaporation ponds were covered with four-layer screen (leveling part, loam – 20 cm, clay – 15 cm, ground-humus mixture – 20cm) with the area of 180000 m^2. Sides of the special ponds were cut in such a way that isolation screen could have a form of three trough–shaped basins where the atmosphere humidity can accumulate as much as needed for a turf formation on the surface in arid climate. Mercury contaminated building structures of the dismantled shop #3 were put (fig. 21-22) in the prepared pit-landfill (with depth of 2.0-3.8 m), the bottom of which was lined with 0.5 m thick anti-filtration screen, and then filled up with ground-cement solution (fig. 23). The structures placed into the pit-landfill formed a concrete monolith which from top was covered with clay-concrete mixture of 0.5 m thick and then with asphalt covering of 6 cm thick. Such burial site of mercury wastes had the following dimensions: 102x155 m including slopes and the total area of 15671 m^2 (fig. 24).

Fig.17. Construction of anti-filtration screen, so called cut-off wall around the building 31

Fig.18. Bucket (grifer) of hydraulic excavator "ЭО-522А"

Fig.19. Construction of anti-filtration screen, so called cut-off wall around mercury waste lagoons

Fig.20. Creation of clay covering above the concrete foundation of the building 31

Fig.21. Piling mercury contaminated building structures into the first compartment of landfill

Fig.22. Piling mercury contaminated building structures into the third compartment of the landfill

Fig.23. Filling in the first compartment of the landfill with ground-concrete mixture

Fig.24. Landfill for mercury waste within the Industrial site #1

For three years the works 860 millions tenge were spent, including 295 millions tenge - in 2002, 242 millions tenge – in 2003 and 323 millions tenge - in 2004. Totally since May 1996 till December 2004 10867.97 thousands tenge were spent in reference prices of 1991 (about $15 millions) which was 1082.56 millions tenge in established prices. After the demercurization program completion the implemented works were approved by State Expert Commission.

State Expert Commission noticed that grounds for making all technical solutions was the results of the special high quality studies and the most efficient integrated decisions were chosen among various possible variants. It was also emphasized that such decontamination project was the first to be implemented throughout the former Soviet Union and it was unique /59/.

4.4. Evaluation of activity efficiency

4.4.1. Field work of 2006

4.4.1.1. Groundwater investigation

Groundwater investigation has been carried out in places of mercury contamination with purpose to receive the data on total and methyl mercury concentration changes.

In June and July, 2006 groundwater samples were being taken from 87 observation boreholes of the system of mercury monitoring at the Northern industrial area of Pavlodar according to the technique developed by AIPET in 2001-2002. Simultaneously with groundwater sampling measurements of water surface, temperature and pH were taken.

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

4.4.1.2. Investigation of soil mercury contamination

Investigation of soil mercury contamination was conducted on the site of demercurization activity of 2002-2004 to assess its efficiency.

19 soil samples were taken at the industrial area of the former chlor-alkali production and in the area of former 6th wastewater pumping station in July of 2006. The samples were taken in places of intensive mercury pollution (the map of mercury pollution with results of monitoring of 2001-2002 was used) from topsoil (0-10 cm) into duple one-use plastic bags.

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

4.4.2. Chemical analytical work

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

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

The rest chemical analytical works were done in AIPET Laboratory in Almaty. The results of the analyses for total mercury of water samples taken from the same three boreholes but at 10

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

4.4.3 Office study

4.4.3.1. Analysis of the results of investigation of groundwater mercury contamination

The results of determination of mercury concentration in groundwater at the area of mercury pollution have been inserted onto the vector map together with the results of similar research of 2004 and 2005 (Fig.25). This map shows dynamic of total mercury concentration change in groundwater in post-demercurization period and allows finding spots with increase in mercury concentration at the area of groundwater mercury contamination plume (due to natural drift of the plume of mercury contamination along groundwater flow) and also spots with decrease in mercury concentration near former building 31 (due to cessation of groundwater recharge with mercury from the source of contamination contained by the cut-off wall). Considerable decrease in mercury concentration near the main hot spot of the mercury contamination allows drawing preliminary conclusion about sufficient efficiency of the taken measures on isolation of the source of mercury contamination located under the former building 31 from groundwater.

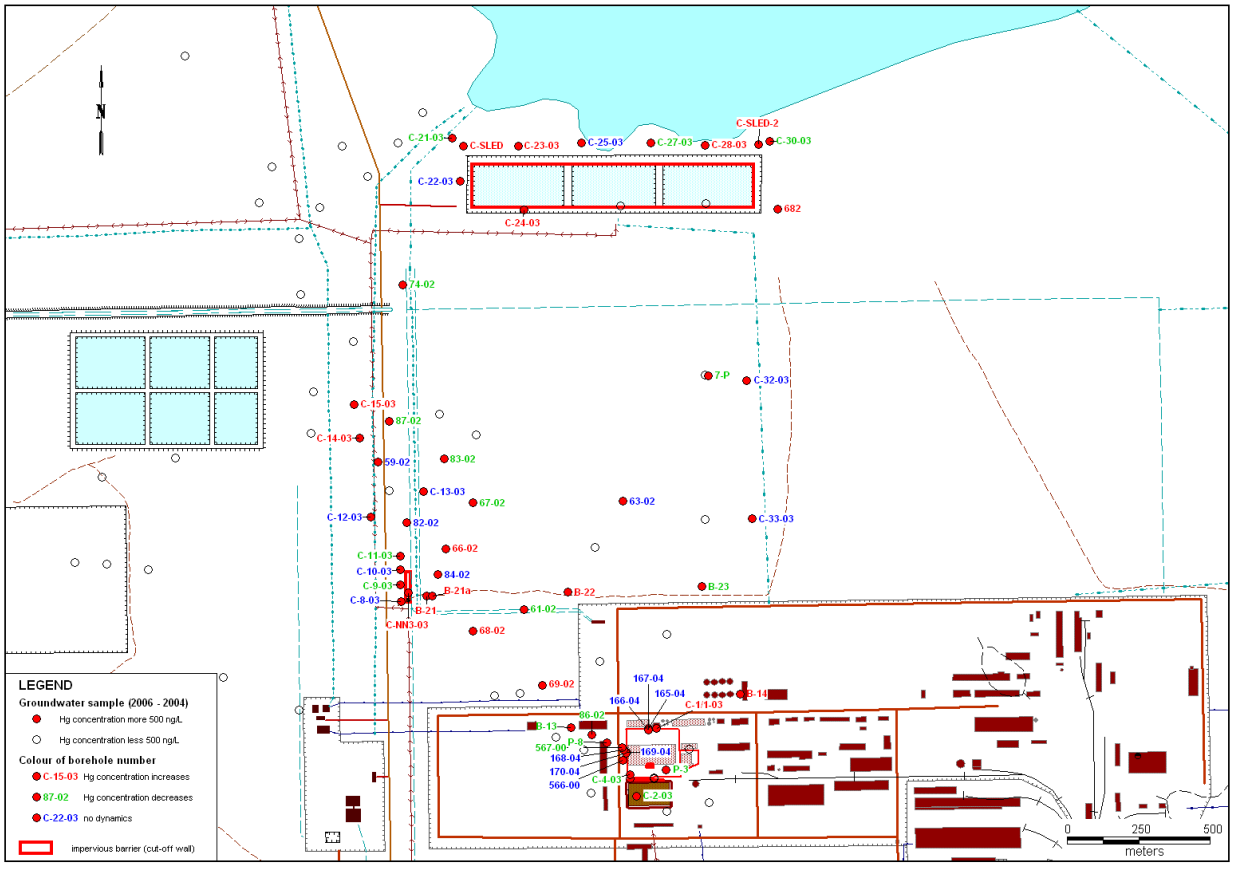

Fig.25. Dynamics of total mercury concentration change in groundwater of the Northern Industrial Area of Pavlodar

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.

4.4.3.2. Analysis of the results of investigation of soil mercury contamination

The results of determination of mercury concentration in soil samples taken within the industrial area of former chlor-alkali production and in site of 6th wastewater pumping station (and also concentrations of mercury vapors) have been inserted onto the vector map of soils mercury contamination, which was produced on the results of 2001-2002 research (fig.26). This figure shows that after demercurization works soil mercury contamination levels here in general are still high (from 2.1 to 95.1 mg/kg at maximum permissible concentration of mercury in soil - MPC_s being 2.1 mg/kg in Kazakhstan) both on the surface of clay caps covering concrete foundations of demolished buildings and within the territory where soils excavation including highly contaminated topsoil digging out was conducted. At that some mercury concentrations can reach extreme values in the order of g/kg.

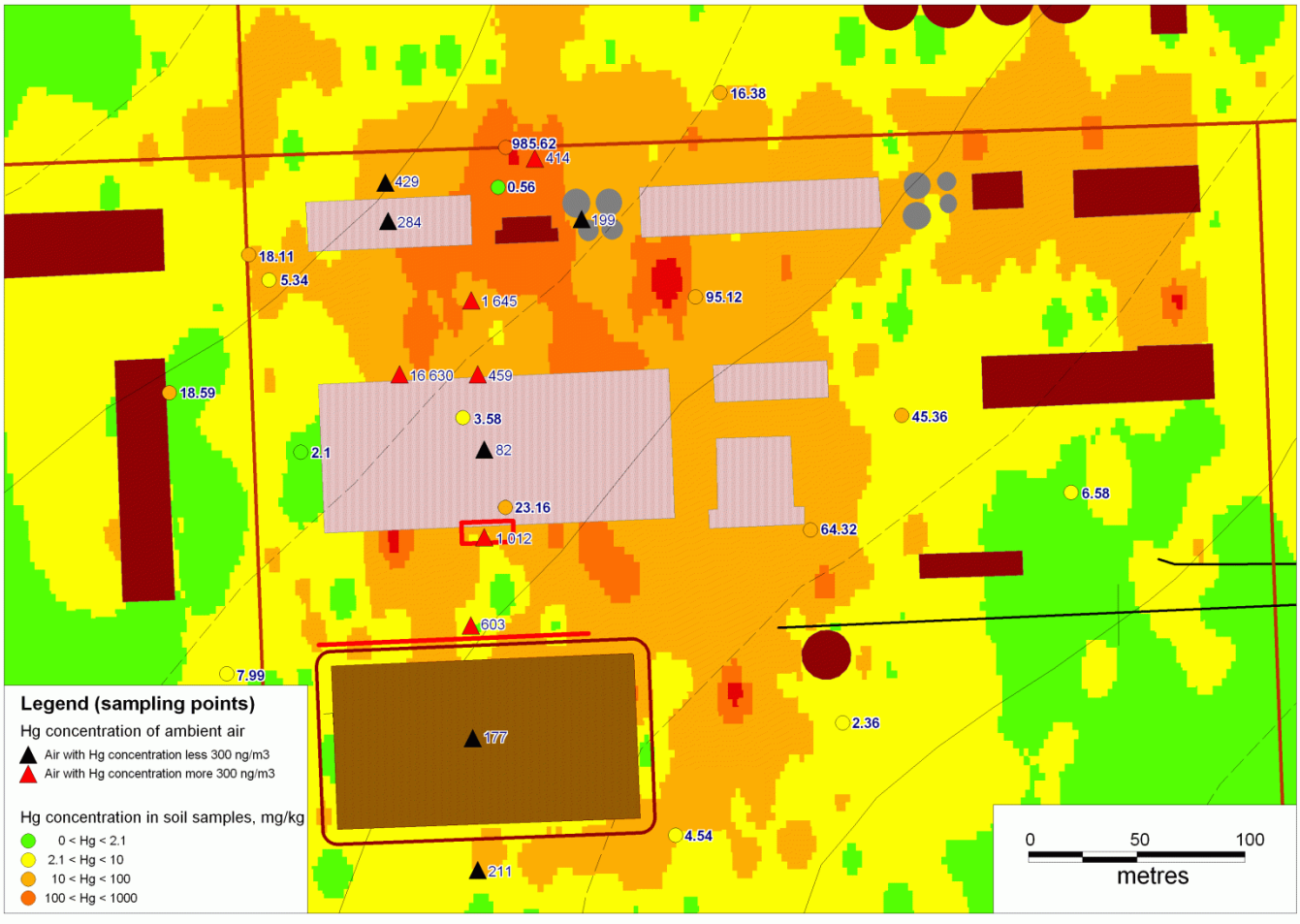

Fig.26. Mercury vapor concentration in near-earth layer of atmosphere and total mercury concentration in topsoil (1-10 cm) in sampling points within the industrial area of PCP in 2006.

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 MPC_{wa} - 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.

Results showed a persistent high level of risk for personnel working at the territory of the former chlor-alkali production posed by soil mercury contamination and the insufficiency of the initial clean up measures taken according to Program of Demercurization in 2002-2004. Persistent soil mercury contamination can in turn entail additional entrance of dissolved mercury into groundwater due to infiltration of atmospheric precipitation through the contaminated layer because this contamination extends beyond the area confined by the cut-off wall.

Measured concentrations of mercury vapors which were about 200 ng/m^3 (on two measuring points) in the center of the landfill for building structures (50 m to the south from the former building 31) and from 100 to 200 ng/m^3 (on four measuring points) on site of special ponds for solid and liquid mercury waste located at south shore of wastewater storage pond Balkyldak proved quite good containment of the mercury waste by these engineering structures.

References

1. Resolution of the Supreme Soviet of National Economy of the USSA of the Council of Ministers of the USSR of November 29, 1963 N 286-p. Moscow, Kremlin. 2 p.

2. I.Levin (Head of Central State Expertise Department of Gosstroi of the USSR). Decision of the Central State Expertise Department of the USSR on the design statement of Pavlodar Chemical Complex construction (Annex to a Letter of Gosstroi of the USSR of September 17, 1963 N 896). 6 p.

3. G.Bozheyeva. The Pavlodar Chemical Weapons Plant in Kazakhstan: History and Legacy. The Nonproliferation Review/Summer 2000, P. 136-145.

4. Regular technological guidelines N2 for chlorine, caustic soda and hydrogen production based on mercury electrolysis in the shop #3 (building #31). Enterprise mail/box B-2174. 1982. 104 p.

5. Regular technological guidelines N3 for treatment facility of mercury contaminated wastewater from the shop #3 of chlorine and caustic soda production on the base of mercury electrolysis. PCP. 1989. 68 p.

6. Regular technological guidelines N26 for thermal mercury regeneration plant in the shop #3. Enterprise mail/box B-2174. 1982. 38 p.

7. A.D.Akhmetov (Director on construction of PCP since 1994 to date). Verbal communication, 23.10.04

8. I.V.Malkov (Foreman of Shop #3 of PCP since1981 till 1984) Verbal communication, 20.10.04

9. B.N.Danevitch, L.S.Uchenik, A.S.Temirbayeva, E.D.Lushin, A.A.Shal, P.I.Glotkin, E.I.Iskakova, L.V.Rylkov. Information on technical status and its impact on environment of the wastewater storage pond Balkyldak, PCP. Pavlodar, November 4-14, 1988 , 7 p.

10. A.S.Korpyakov (Director of PCP). Information on dams' construction progress at the wastewater storage pond Balkyldak as of November 1, 1976, 4 p.

11. E.N.Lushin, T.E.Krakhaleva, A.F.Krakhalev. Results of study of mercury contamination at the industrial site of chlorine and caustic sida production at PCP (Final report). Science and Technology Center "Tekhnolog", Pavlodar, 1990, 194 p.

12. E.P.Serenyuk (Director of PCP since 1997 till 1998). Verbal communication, 23.07.04

13. B.A.Sharov (Director PCP since 1988 till 1997). Verbal communication, 28.09.04

14. V.A.Skripnik, A.A.Uzbekov, A.Yu.Noel, M.I.Korshun. Report "Results of study of structures of the production's buildings mercury contamination levels constructions, calculation of the class of toxicity of above-ground parts of the buildings. Development of recommendations on burial of waste of contaminated buildings' structures and demercurization of shops". KNIF GosNIIKHLORPROYEKT, Kiev, 1989, 39 p.

15. V.A.Skripnik, V.I.Barmashenko, M.N.Korshun. Recommendations on demercurization of equipment and burial of wastes from chlorine and caustic soda production based on mercury method at PCP. KNIF GosNIIKHLORPROYEKT, Kiev, 1989, 41 p.

16. L.E.Postlov, I.I.Drel. Report on the project "Development of wasteless processes of wastewater and gas emissions treatment from mercury, technology of mercury removal from soil of industrial sites of mercury electrolysis. Pilot trials of the process". KNIF GosNIIKHLOR-PROYEKT, Kiev, 1990.

17. V.I.Skripnik, A.A.Uzbekov. Initial data and recommendations on elimination of mercury contamination of soils in industrial site of chlorine and caustic soda production based on mercury method at PCP. KNIF MNPO "Sintez", Kiev, 1991, 43 p.

18. A.A.Uzbekov, A.Yu.Noel, V.P.Zolin. Recommendations for environmental protection against mercury contamination. KNII "Cinteko". Kiev, 1992, 22 p.

19. M. Sh.Ishankulov, A.D.Saltybayev. Report "Snow cover contamination in Pavlodar and its vicinity with chemicals". Health Center of Ministry of Health, RK. Almaty, 1991. 5 p.

20. M.Sh..Ishankulov, A.D.Saltybayev. Report "Study of present status of man-made contamination of soil, drinking water, vegetation and food products in Pavlodar". Health Center of Ministry of Health, RK. Almaty, 1992. 7 p.

21. M.A.Ilyushchenko. Report (final) on research in the framework of fundamental study "Development of atomic-absorption methods of mercury determination and forms of its occurrence in environmental objects and assessment of mercury man-made geo-chemical anomalies extend in Central and Northeast Kazakhstan. KazGU, Almaty, 1996. 102 p.

22. A.D.Saltybayev. Geochemical peculiarities of system "ambient air – soil – groundwater – vegetation" in the condition of industrial contamination of Pavlodar. Abstract of PhD thesis. Almaty 1995. 23 p.

23. N.M.Khlystun. Ecologo-chemical study of nature environments condition in Pavlodar – Ekibastus regional industrial complex. Abstract of PhD thesis. Almaty 1999. 28 p.

24. T.I.Slazhneva. Environmental Impact Assessment (EIA) of PO "Khimprom", Pavlodar. Health Protection Centre, Ministry of Health RK. Almaty, 1992, 433 p.

25. I.M.Kamberov, M.I.Politikov. Report on the project INTAS-Kz 95-19 "Study of environment around Pavlodar" for 1997-1999. Almaty, Dublin 1999. 50 p.

26. T.W.Tanton, S.M.Ullrich, G.Zh.Daukeev, M.A.Ilyushchenko, E.V.Lapshin, V.V.Veselov, V.Yu.Panichkin, I.M.Kamberov. Results of researches on mercury contamination in the north industrial area of Pavlodar and proposals on its demercurization. Proceedings of III International scientific conference "Heavy metals, radionuclides and biophilic elements in an environment (Semipalatinsk , 7-9 October 2004.)". Semipalatinst State Pedagogical University. Semipalatinsk 2004. V.1. p. 72-77.

27. T.W.Tanton, V.V.Veselov, M.A.Ilyushchenko, V.Yu.Panichkin. Assessment of risk posed by mercury contamination in the Northrn industrial area of Pavlodar. Reports to the National Academy of Sciences, RK. N4, 2003, p.78-81.

28. L.E.Postolov, I.I.Drel. Demercurization of decommissioned production of chlorine and caustic soda. Working design. General explanatory paper. JV "Evrohim", Kiev, 1995, 89 p.

29. Feasibility Study report on process conversion project for chlor-alkali plant of Chimprom, Pavlodar in Republic of Kazakhstan. Japan Consulting Institute. November 1993. 119 p.

30. M.A.Ilyushchenko. Report on Agreement N134 (US 37/2003n) of 21.08.2003 «Development of mercury monitoring program in the Northern industrial area of Pavlodar" AIPET, Almaty 2004. 37 p.

31. V.V.Sokolov, V.S.Mochulskiy, V.V.Kuznetsov. Main regulations for demercurization of equipment and building structures, elimination of soil's mercury contamination of the territory of the shop #31 at PO Khimprom, Pavlodar. Institute Giprosintez, Volgograd, 1992, 10 p.

32. L.E.Postolov. Initial data for design of the process of neutralization and burial of mercury containing materials at PO Khimprom, Pavlodar during demercurization works. JV "Evrohim", Kiev, 1995, 31 p.

33. Report on the project "Development of concrete mixture composition, way of its preparation and placement into cells of storages with selection of compositions and testing samples of fine-grained ground-concrete based on Portland cement as astringent". Kiev State University of Construction and Architecture, Kiev, 1995.

34. E.N.Lushin. Preliminary conclusion on the results of study for identification of landfill for mercury containing materials at the industrial site of PCP. JSC "Pavlodargidrogeologia", Zhetekshi. 1995.

35. Protocol of the meeting of MNREP RK with the BRGM representative Georges Morisot (France), Kokshetau, 03.08.1999. 2 p.

36. Protocol of the BRGM meeting "Demercurization project in Pavlodar: EIA and elimination of the contamination hotspots", Pavlodar, 24.04.2000. 3 p.

37. Protocol on financing between French Republic Government and the Government of the Republic of Kazakhstan. 05.10.2000. 4 p.

38. Protocol of talks on realization of the project "Demercurization activity and identification of mercury contamination hotspot in Pavlodar", Kokshetau, 10.11.2000. MNREP RK. 3 p.

39. A.B.Freiberg, Acting Chairman of Committee for Environment Protection in MNREP RK. Assignment for development of FS "Demercurization activity and elimination of mercury contamination hotspot in Pavlodar". 16.11.2000. 2 p.

40. A.D.Akhmetov, Director on construction of PCP, Comparative chart of proposals on elimination of mercury contamination hotspot at JSC "PCP", developed by JV Evrohim and French Company BRGM. 2001. 3 p.

41. Letter of JSC "PCP" President E.M.Nurpeisov, Chief Engineer L.K.Shchetinin, Director on Construction A.D.Akhmetov to Akim of Pavlodar oblast G.B.Zhakiyanov N 71-05-96 of 26.01.2001. 2 p.

42. L.E.Postolov, I.I.Drel. Demercurization of decommissioned chlorine and caustic soda production based on mercury method. Correction of Working Design. General explanatory note. JV Evrohim, Kiev, 2003, 71 p.

43. L.E.Postolov, I.IDrel. Technical decisions on burial of mercury containing wastes in compliance with Working Design (1995) and correction of Working Design (2003) "Demercurization of decommissioned chlorine and caustic soda production based on mercury method at JSC "PCP". JV Evrohim, Kiev. 2004. 15 p.

44. A.D.Akhmetov, L.E.Postolov, M.A.Ilyushchenko. "Assignment on development of correction of Working Design "Demercurization of decommissioned chlorine and caustic soda production". 2003. 2 p.

45. A.Verbnyak, V.Bednenko, G.Voronin, A.Akhmetov, L.Postolov. Protocol of the meeting with V. Bednenko, Head of Pavlodar Oblast Environmental Territorial Authority on Environmental Protection devoted to correction of the project of demercurization at JSC "PCP". July 23, 2003. 2 p.

46. L.E.Postolov and I.I.Drel (authors of JV Evrohim's design of demercurization of chlor-alkali production of PCP). Verbal communication, 20.08.04

47. Program of demercurization of decommissioned production of chlorine and caustic soda based on mercury method at JSC "Khimprom". Pavlodar JSC "Khimprom", Pavlodar, 1998. 15 p.

48. L.K.Polezhayev (Governor of Omsk oblast, RF). Letter to RF Government Chairman Mr. S.V. Stepashin N 1-01/217 of 23.06.99. 2 p.

49. Yu.V.Knyazev (Head of Industrial Laboratory of Sanitary Epidemiological Agency of Pavlodar. Sanitary order No. 26-08-147 of 17.08.98. 1 p.

50. V.I.Lyagushnikov, V.N.Kvashnin, N.A.Parfenov, S.N.Sultanbayev, M.Sh,Akhmetov, D.G.Tashimova. Act of collection and acceptance of 3993 kg of metal mercury to the storage #9. 23.11.1998. 1 p.

51. V.Keremkulov (Chairman of the Committee for the Environmental Protection, Chief State Inspector of RK). Letter N 1/353 of 22.04.99 to A.G. Siryk, a President of JSC "Khim-prom" 2 p.

52. V. G.Gurdzhei, P.A.Dubok, V.I.Tereshkov, B.K.Serzhanov, N.M.Khlystun. Protocol of the meeting of representatives of committees, authority of Omsk and Pavlodar oblast administrations on the problem of the Irtysh River mercury pollution . Pavlodar, April 28, 2000. 6 p.

53. A.G.Siryk, L.K.Shchetinin, A.D.Akhmetov, E.P.Serenyuk, S,Yu.Sokol, A.V.Kasyanenko, K.V.Khortsev. Protocol of technical meeting of JSC "PCP" on demercuriza-tion of dismantled equipment of Shop # 31. Pavlodar, 3.05.1999.1 p.

54. N.Leontyev (Deputy Head of Pavlodar oblast environmental department). Decision of state expertise on the temporal storage of mercury decomposers in the cell #1 of screened special evaporation ponds. Letter to JSC "PCP" N1/431 of 19.05.1999. 2 p.

55. A.V.Ryumin (First Deputy Oblast Akim). Assignment of Oblast Akim G.B. Zhakiyanov while visiting JSC "PCP" in May 18, 1999.1p.

56. K.Aitekenov (Chairman of Committee for Environmental Protection of RK) Chronology of the demercurization project "Demercurization activity and elimination of mercury contamina-tion hotspot in Pavlodar" implementation in Pavlodar. (Note to Vise Prim Minister, Ministry of Finance RK A.S. Pavlov). 23.02.2002. 6 p.

57. E.Trusov (Director of Pavlodar oblst of Environmental Fund), A. Akhmetov (Director on construction at PCP). Information on implemented demercurization activities at decommis-sioned production of chlorine and caustic soda based on mercury method at JSC "PCP". 2002. 1 p.

58. N. K.Autalipov, I.I.Drel, E.K.Nacharova, A.D.Akhmetov, N.V.Solovyova, G.S.Manyakhin, B.A.Sardarov, V.A.Migachov, K.Zh.Beisebayev, A.M.Karabalin, B.K.Shapkenov, S.K.Matviyenko, Zh.A.Usenov, A.Zh.Bikenov. Conclusion of working com-mission (assigned by the order of the Department of Environmental Programms of Pavlodar oblast, N21 of 16.11.2004) about receiving the object ready in order to be presented to the State Acceptance Inspection. December 7, 2004. Pavlodar,6 p.

59. Zh.Zh.Nurgaliyev, I.I.Drel, S.S.Abeldinov, E.V.Skarov, V.A.Bednenko, S.A.Adamzhanov, Zh.Sh.Aliyev, T.K.Kamashev, B.K.Shapkenov, A.D.Akhmetov. Act of State Acceptance Inspection (assigned by Akim of Pavlodar oblast decision N27 of 29.11.2004) on acceptance of constructed object and its commissioning of December 25, 2004. Approved by the oblast Akim decision of February 28, 2005. Pavlodar, 5 c.

Abbreviations

AIPET – Almaty Institute of power Engineering and Telecommunications
AAS - atomic absorptive spectrophotometer Lyumex RA 915+ (Russia)
BG – [BG Group] BG Company, Great Britain
EIA - Environmental Impact Assessment
EPA – [US EPA] Environmental Protection Agency, USA
fig. – figure
FS - Feasibility Study
GDR – German Democratic Republic
GeoDelf - Consulting Company "GeoDelf", Netherlands
GIS - Geographic Information System
GPS – Global Positioning System
IHH - Institute of Hydrogeology and Hydrophysics, Ministry of Science and Education, RK, Almaty
IMV – Institute of Microbiology and Virology of Ministry of Education and Science, RK,
INCO – Specific International Scientific Cooperation Activities
INS – Institute of Natural Science, Almaty
INTAS – International Association for the Promotion of Co-operation with Scientists from the NIS
ISTC – International Science of Technology Center
JSC – Joint Stock Campony
JV "Evrohim" - joint venture "Evrohim", Kiev
KazGU - Research Institute of New Technologies and Materials at Al-Farabi Kazakh state National University, Almaty
KNIIF GOSNIICHLORPROEKT – Kiev Research Branch of State Research Institute "Chlor-Project"
KNIF MNPO "Sintez" - Kiev Research Branch of International Research Association "Sintez"
KNII "Sinteko" - Kiev Research Institute "Sinteko"
Ltd. – company with limited liability
MNREP RK - Ministry of National Resources and Environmental Protection of the Republic of Kazakhstan
MPC_{da} - Maximum permissible concentration in air daily average, equal to 300 ng/m^3 for mercury
MPC_w - Maximum permissible concentration in water of a water body equal to 500 ng/L for mercury
MPC_f - Maximum permissible concentration in fish: 0.6 mg/kg for mercury in predatory fishes and 0.3 mg/kg for mercury in non predatory fishes
MPCs - Maximum permissible concentration in soil equal to 2.1 mg/kg for mercury
MPC_{wa} - Maximum permissible concentration in air of working area equal to 10000 ng/m3 for mercury
NGO – Non Government Organization
NII- Research Institute
NIS - New Independent States
PCP – Pavlodar Chemical Plant
pH – hydrogen ion exponent (characteristic of acidity and alkalinity of aqueous solution)
PHH - Pavlodar Hydrogeological Expedition – Science and Technology Centre "Technolog" Almaty
PO – Production Association
Pond Balkyldak (Balkyldak) – wastewater storage pond (former natural lake) Balkyldak
POR – Pavlodar Oil Refinery

PSU - Pavlodar State University
QA/QC –Quality assurance and quality control
Red-ox potential – reduction–oxidation potential in a solution
RF – Russian Federation
RK – the Republic of Kazakhstan
SLM - Stepnogorsk Laboratory of Monitoring
Special ponds - special evaporation ponds for liquid mercury containing wastes (they also were used as a storage for solid mercury containing wastes)
SSEU - Siberian Spiritual-Ecological University, Omsk, Russia
SU - Department of Civil Engineering of Southampton University, Great Britain
TES - urban power station generating also steam for heating.
USA – United States of America
USSR – Union of Soviet Socialist Republic

SPECIFIC SUPPORT ACTION

BIOMERCURY

Worldwide remediation of mercury hazards through biotechnology

NMP2-CT-2004-505561

Priority 3 NMP: Nanotechnology and nanosciences, knowledge based multifunctional materials, new production processes and devices

Deliverable D7

Case study report on Vlora hot spot of pollution

Deliverable due date: PM 30
Actual submission date:PM 30

Start date of project: 01/03/2004 Duration: 36 months

Lead contractor: **University of Tirana, Albania**

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	✓

Worldwide remediation of mercury hazards through biotechnology

Case Study 2: WP2 Hot Spot of Pollution (Vlora, Albania)

(Workpackage 2: Hot Spot of Pollution, Vlora, Albania)

Participant
CR 8 University of Tirana UT-LACH Albania 1 36

Report on "Vlora Hot Spot" pollution

Deliverables
D5 Report on pollution including own data, published and unpublished data

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CONTENT

CHAPTER 1 GENERAL VIEW

Vlora, with a population of about 120 000 habitants, is the biggest city positioned in South-West part of Albania; located on the gulf carrying the same name. Vlora Bay presents the natural boundary between the Adriatic Sea and the Ionian Sea and has a wonderful view and beach.

Figure 1 The map of Albania

Four kilometers north of the city is the site of a former chemical complex including also a chlorine-alkali plant, see figure 2.

Figure 2 The view of Vlora city

Soda-PVC Plant is positioned 5 km far from Vlora City (North Direction) and about 4 km far from Narta Lagoon (South-West Direction), in an ex-industrial area. It was build up in a sandy area, along a coastal forest, following the Vlora-Zvernec (Narta) Road. Some other industrial plants have been in this area, like The Plant of Electric Lamps, Mechanical Plant, Food Processing Complex Plant, The Plant of Soap Oil, etc. Soda – PVC Plant lie down in an area of about 20 ha, its surface of 9 ha belongs to PVC Plant. There is another area of 25 ha used as technological dump's disposal, positioned between the Plant and the coast.
Soda-PVC Plant started its normal production of caustic soda and alkali soda on February 1967. Ten years later (November, 1976), PVC Plant started its normal production. Its main products were caustic soda (using ammonia's method), soda (using limestone method) and PVC (using the method of polymerization of liquid monomers). The reaction between liquid C_2H_2 and HCl (using $HgCl_2$ adsorbed to active carbon as cathalizator) was used during the monomer's producing. Mercury was used too, as the cathode during the process of the electrolysis of NaCl in electrolysis baths. The periodical cleaning of the baths and of the filters of activated carbon caused the mercury pollution of the area during the operation of the plant.
About 1620 employees (40% of these are women) had been working there during the operation of the plant.

The plant was closed in 1992, and its buildings have been completely destroyed since that time.

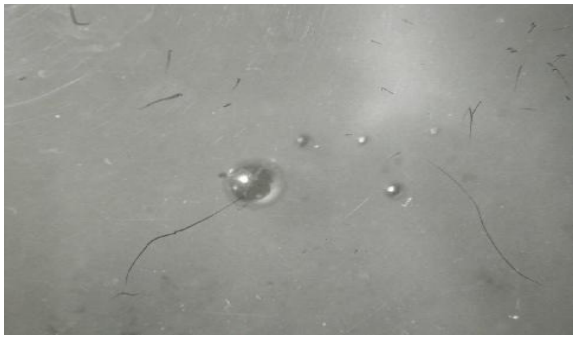
Figure 3 The views from the destroyed factory

During its operation (1976-1992) liquid wastes of about 500 m^3/hr containing 1.1 mg/L mercury were discharged without any treatment directly into the sea. The polluted sludge were deposited on an open damp (25 ha) very near seashore. The quantity of mercury discharged in the environment during period 1977-1983 was estimated about 65 tons[1]. The problem of Hg pollution is still stand present in Vlora city, Albania, just in the site of former chemical complex that produced chlorine alkali, vinyl chloride monomer and polyvinyl chloride.

The soil territory of about 50,000.00-60,000.00 square meters of the former plant is contaminated with mercury to a depth 1.0-1.5 meters below ground level. Very high levels of mercury vapor are detected in the atmospheric air. The factory encompasses approximately one km^2 and is located directly on Adriatic Sea.

From former investigations, drops of metallic mercury in the hall of the electrolysis plant and in all of its drainage canals were observed.

Mercury content levels > 10,000 mg/kg [18] in the area of the former plant is 1,000 times greater than typical EU thresholds. Between the former plant and the Sea there is an area formerly used for the disposal of the factory's industrial wastes, which is also highly polluted.



180 families living now on and around the industrial site. The area presents an unacceptable threat to the environment.

Marine sediments and water samples collected near the plant area show also high levels of mercury. On July 2002, a mission of UNEP/MAP (GEF Project GF/ME/6030-00-08) had identified this area as a "hot spot" and a pre-investment

study “Environment Remediation Project for Vlora Hot Spot in Albania” is in course of preparation.
The aim of this report is to present some of the most important results of our studies for mercury contamination in the area of ex-Chlor Alkali Plant and Vlora Bay [2, 3, 4, 5, 6, 7, 13, 15, 16].

CHAPTER 2 THE GEOLOGY AND GEOPHYSICS OF THE AREA

The area of interest is situated on the coast of Adriatic Sea. It belongs to the Vlora plain. The sea-level altitude is given as 0.5 – 1 m by a local elevation of 1 – 2 m above the sea level. The chemical plant SODA is built on the surface elevation [21].

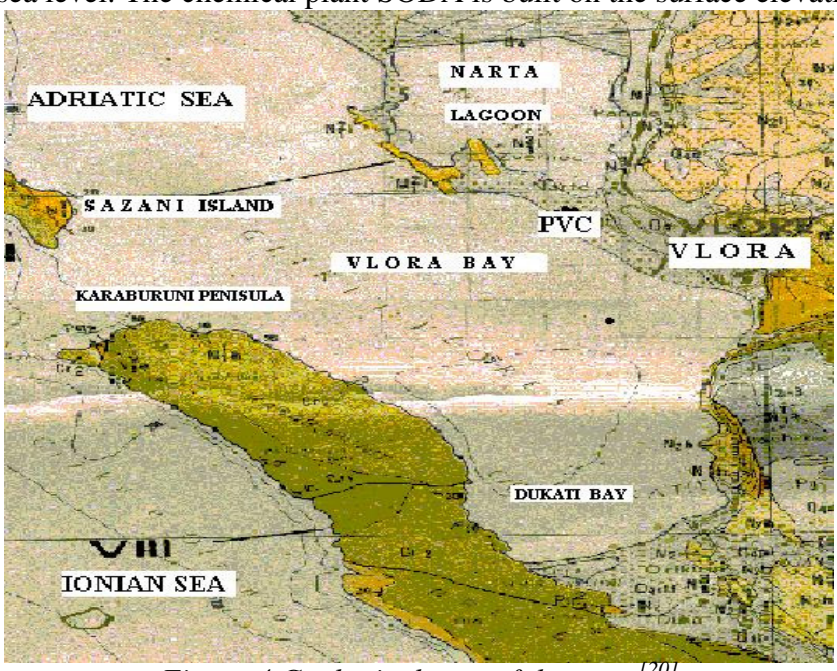


Figure 4 Geological map of the area [20]

The geological formation of the area consist mostly in carbonates formation[20] (Cr_1, Cr_2, N_1^1, Pg_3^2), associated by a mixed formation of carbonates (about 90%), sandy and sandy rocks (≅10%) ($N_1, N_2, N_3, N_1^2, N_1^3$). The sediments of this area are mostly as calcium carbonates, Q4.

For ganging the concept on the tectonic structure of Vlora area, a photo of the ground surface made by the Land sat 7 satellites were analyzed from Geotest [21]. From the photos made by satellite (6 photos made on March, 200) an interesting hydro-geological aspect were deduced: water currents in the open sea of Vlora Bay (blue, green, red bands are evident in photos). The fine material brought to the sea by Vjosa River is carried from the river mouth by the sea currents to the South. The light color of the water, which bears fine clayey particles, indicates that the load materials do not

reach the Vlora Bay. It is highly possible that the sea currents flowing along the coast take away the materials farther to the sea. The loaded materials reach the area between the Sazani Inland, Karaburuni Peninsula and the open Adriatic and Ionic Sea. A number of tectonic structure series, as well as of dislocation system perpendicular to the basic geological direction of the region N – S and a lot of pinnate faults, were evident from the photos.
Through geophysical investigation [21], high specific resistance was observed. The specific resistance of the surface layer were in the ranges of ten ohmmeters to the first tens of thousands ohmmeters. The surface high-resistively layer consists mainly of unsaturated sands, that involve man-made layers, concrete, building debris and so on in the area of the factory. Due to the high salt content in some locally area or the existence of some individual formation of Quaternary sediments, within the surface layer, some low specific resistance places were found [20]. The depth to the upper boundary of the "salty sands" is 4 – 16 m

CHAPTER 3: ANALYTICAL PROCEDURES

3.1. Sampling Procedure

3.1.1. Seawater samples were conserved on PET bottles and after filtration through OSMONIC INC, glass filter (1.0 micron) were acidified with 1ml/L HNO_3 solution and stored at 5°C.

***3.1.2. Sediment samples*:** The fractions smaller than 2 mm of the sediment samples were well homogenized by grinding in agate mortar until all material was going through a 200 μm nylon sieve. Sub sample for mercury determination was dried at 50-60 ^{0}C. After drying, the samples for chemical analyses were stored in airtight plastic vials until required for future use.

3.1.3. Soil samples were collected up to 15 cm deep from the surface, were air dried, sieved through a 2.0 mm screen, and then grounded and sieved through a 0.063 mm screen. The homogenized samples were stored in airtight pure plastic bags until used for chemical analyses.

3.1.4. Biota samples was carefully washed with full distilled water for several times, till the water remain clear, dried at room temperature for 2 days, grinded by an electric grinder, dried again at 60^{0}C for 3 hours.

3.1.5. Hair samples: A questioner was prepared in order to collect data, such as age, sex, the time of mercury exposure, the manner of hair treatment, the frequency of fish consuming, etc. hair strands from each participant were collected from the root in the occipital region and was placed in a closed plastic bag.

3.2. Analytical Procedure

3.2.1. Analytical Procedure of seawater samples

Analysis was performed on 100-200 mL seawater samples. The sample was transferred to a 250-mL seperative flask, together with H_2SO_4 (15 mL), KBr solution (2%, 2 mL), and toluene (10 mL). After stirring for 1 min the organic phase was collected and NH_4Cl (2%, 2 5 mL) was used for re-extraction of mercury from the organic phase.

The aqueous (inorganic) phase was collected for determination of total and inorganic mercury [7].

***3.2.2. Analytical Procedure of sediments and soil samples*:**
A procedure based on UNEP/IAEA Reference Method for Pollution Studies [17] was used. A 0.3-0.5 g sub sample was treated with a mixture of HNO_3+HCl (9:1) in a hot plate at 70-80 ^{0}C for 3 hours in closed PTFE vessels. After cooling, 1 ml of 5% $K_2Cr_2O_7$ was added and water up to 50 ml. Depending on mercury content in the sample, an aliquot of clear solution was used for mercury determination by Cold Vapor Atomic Absorption Spectrometry (CV-AAS). All measurements were carried out using a Varian SPECTRAA 10 Plus instrument equipped with a home-made schema having sensitivity about 0.2 ppb Hg. All reagents used for mercury analyses are "low in Hg" quality (from Merck).

***3.2.3. Analytical Procedure of biota samples*:**
0.3-0.5 g sub sample is treated with a mixture of HNO_3+HCl (9:1) for 24 hours in room temperature in half pressure PTFE vessels. Than the samples was treated in a hot plate at 70-80 ^{0}C for 3 hours. After cooling, 1 ml of 5% $K_2Cr_2O_7$ is added and water up to 50 ml. Depending on mercury content in the sample, an aliquot of clear solution is used for determination of mercury content by Cold Vapor Atomic Absorption.

***3.2.4. Analytical Procedure of hair samples*:**
The hair samples were washed with warm 0.25% dodecyl-sodium salt (detergent solution) in 100 ml beakers, rinsed several times with distilled water and finally with a small portion of acetone. The samples were air dried till about 5% of weight difference between two sequential weighting. Dry weight results were reported.
Several digestion methods were focused for sample digestion procedure for total mercury determination. 0.1-0.3 g hair samples and 6 ml “Aqua regia” ($HCl:HNO_3$=3:1) were mixed together in half pressure Teflon vessels. After overnight digestion at room temperature, the samples were digested for three hours at 80-90^0 C. 1 ml 5% $K_2Cr_2O_7$ was added and the samples were digested again for two hours increasing temperature gradually to 150^0 C. The samples were past to 50 ml volumetric flask and were diluted to the mark with distilled water.

3.2.5. The determination of Mercury
CVAAS technique was used for mercury determination.
The system used for volatilization and atomization of mercury is shown schematically in Fig. 5 [7]. A small gas wash bottle was used as the reaction flask for extractive determination (Fig. 1). The air used as carrier and mixing gas was introduced through a gas frit near the bottom of the gas wash bottle. The optimum conditions for the cold vapor system were sample volume injected 20 ml and air carrier gas flow rate 2.0 L/min.

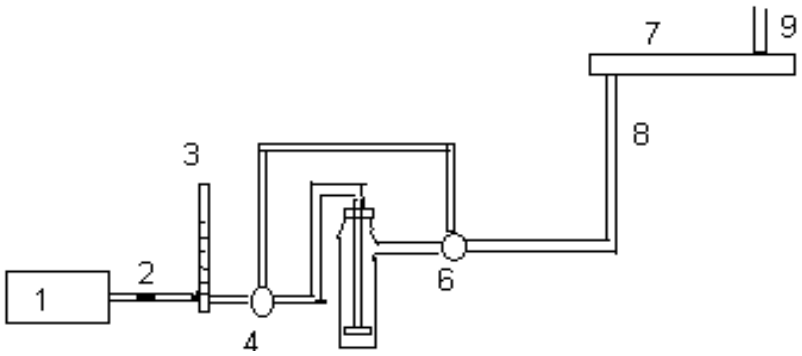


Figure 5. *Schematic diagram of the system used for volatilization and atomization of mercury:*
1. Air compressor, 2. Air cleaner, 3. Air flow meter, 4. Recorder, 5. Wash air entrance, 6. Gas wash bottle, 7. Quartz cell, 8. Hg vapor entrance, 9. Hg vapor exit

3.2.5.1. Reagents

All reagents were of analytical grade and met the requirements for determination of mercury. Tin(II) chloride was used as a 10% solution in HCl for reduction of Hg^{+2} to Hg^0. The solution was purified in the gas wash bottle for 10 minutes with airflow of 2.0 L/min.

3.2.5.2. Operation of cold vapor system

Samples ready for determination of total, inorganic, or organic mercury were transferred to the gas wash bottle and $SnCl_2$ solution (10 mL) was added. Gas flowing from the bottom of the bottle transferred mercury (Hg^0) vapor through the measuring quartz cell, mounted in the optical path of the apparatus. After signal recording the stream of gas was changed to cleaning mode and the system was ready for next measurement. The signal from standards was measured by the addition method, after removal of mercury vapor from the sample. Blank samples were prepared from distilled water and treated in the same way with natural samples.

3.3. Quality assurance of the data

Two reference certified materials (CRM) were analyzed at the same time with sediment samples of studied area, SDM/2-TM and IAEA 405 purchased from IAEA Monaco. It could be noticed that data obtained were in good agreement with certified values.
A reference certified materials (CRM), IAEA 086 and an inner standard prepared in our laboratory, were analyzed at the same time with our samples of studied area. It could be noticed that the data obtained were in good agreement with certified values.

CHAPTER 4: THE CONTAMINATION LEVEL OF "VLORA HOT SPOT POLLUTION"

4.1. Mercury in Soils

4.1. 1. Hg content in soils

Two monitoring field works were done during the years 1999-2001 in territory of former clor-alkali plant for mercury level valuation from Tirana Chemical Institute in collaboration with Analytical Chemistry Section of University of Tirana. 113 surface soils were collected (15 cm deep from the surface level) for monitoring inside territory of the plant and in its periphery. A map of Hg levels in soils of former chemical plant has been prepared using the results of these 113 surface (up to 15 cm) soils[13]. The results are given in table 1.

Table 1 Hg content in surface soils (collected 15 cm deep) (in mg/kg, DW)

No.	*Plant*	*N*	*Average content,* $\bar{X}$	*Range*	*LQ-UQ (10 to 90 %)*
1	*Electrolysis*	57	311.8	0.9 – 2470	28.8 – 409
2	*Polymerization*	10	398.3	1.2 – 1900	4.1 – 718
3	*Oxygen*	8	10.6	0.5 – 37.4	2.2 – 17.0
4	*Acetylene*	6	5.12	0.8 – 13.1	1.8 – 7.9
5	*Others*	32	84.3	0.1 - 1260	0.7 – 21.8

LQ – lower quartile, UQ – uper quartile

The content of mercury found in the area was varied from 0.08 mg/kg (DW) to maximal value of 2472 mg/kg (DW); with the mean of 205.6 mg/kg. 90% of the samples have mercury content 1.8 to 165.8 mg/kg (DW). More than the half of total number of the samples presents Hg concentrations more than 20 mg/kg (the limit of polluted samples in Great Britain). About all samples show concentrations more than 0.07-0.3 mg/kg, which the "preliminary critical limits to prevent ecological effects" is according UNEP Chemicals [12].

The most contaminated territory is Electrolysis Plant (mean concentration of mercury was 311.8 mg/kg (n=57), maximum level 2472 mg/kg) and Polymerization Plant (398 mg/kg (n=10), maximum level 1900 mg/kg). The content of mercury decreased in exponential way ($\log c = -0.0198\, d + 4.94;\ r = -0.73;\ n = 113$) as the distance from Electrolysis Plant increased. The content of mercury in soils was going to increase in West direction of the pant (direction of seashore). May be it related with transport of mercury by erosion process during the raining period. The transport of mercury from the soils to seawater and sediments is a long process, which should continue for many years. The contaminated soils are potential sours of contamination of the area.

Figure 6 View from the contaminated soils

The third monitory field works[19] were done during the years 2001 - 2003 in territory of former Chlor-alkali Plant for mercury level valuation from Geotest, Brno, Czechk Republic. The results are illustrated in map given in figure 6.

In determining mercury in soils, the attention was focused on the areas with high mercury concentration in soil air. Soils samples were collected from unsaturated zone at different depth level (0.0, 0.5, 1.0, 1.5 m and if it was possible to 2.0 m using a manual pedological probe and a manual earth auger for sampling. The area was divided in three zones: Zone I- The most contaminated site of PVC Plant; Zone II – the territory between PVC Plant and Adriatic Sea, where the lump sludge was dumped; Zone III – The territory between PVC Plant and pine forest, where the wastes were dumped. The area extent of contamination in individual depth levels is given in table 2. These data will serve to estimate the volume of the soils to be excavated in dependence with fixed limit.

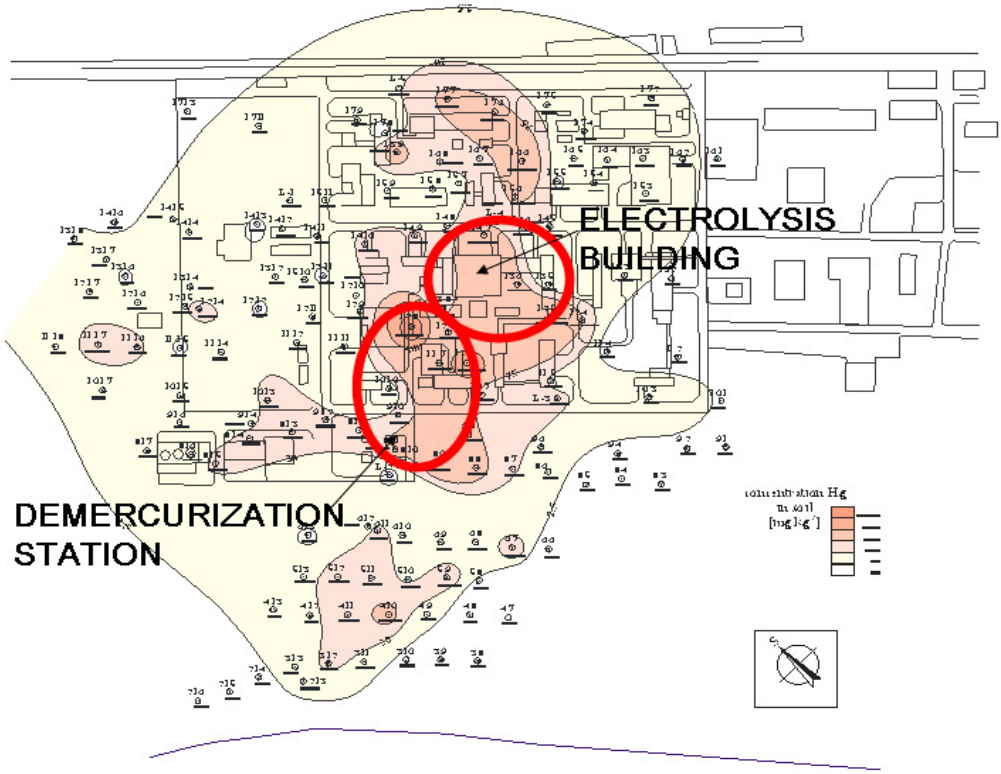


Figure 7 The map of Hg distribution in soils

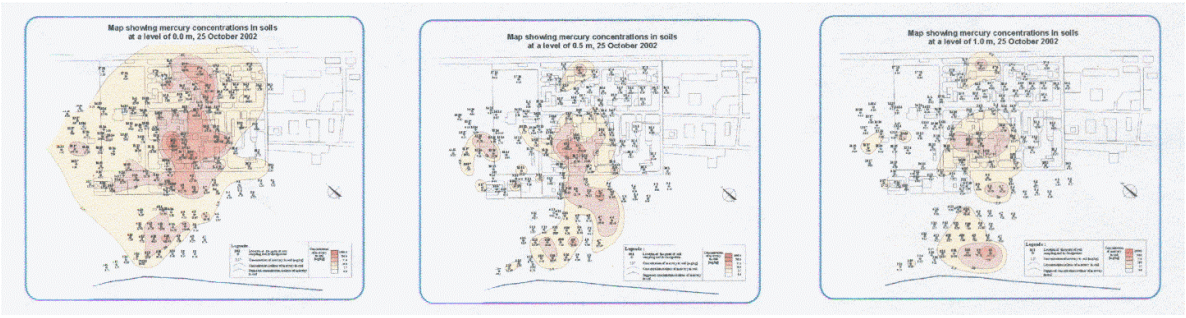


Figure 8 The map of Hg concentrations in soils in Five Depth Levels

Table *2 Area Extent of Hg Contamination in Five Depth Levels*

Depth	*Area I*		*Area II*		*Area III*	
	C>20 mg/kg	*C>75 mg/kg*	*C>20 mg/kg*	*C>75 mg/kg*	*C>20 mg/kg*	*C>75 mg/kg*
(m)	(m2)	(m2)	(m2)	(m2)	(m2)	(m2)
0	41,600	17,680	5,500	60	1,320	-
0.5	17,800	2,260	1,580	120	2,000	-
1	6,400	175	6,320	880	240	-
1.5	5,350	200	1,320	-	-	-
2	-	-	240	-	-	-

Table 3 The volume of the soils to be excavated in dependence with fixed limit

Soil (C>20 mg/kg)	Area I (m3)	Area II (m3)	Area III (m3)
Volume*	25,175	6,105	1,455

The dedected vertical distribution of Hg in the area of concern reveals that the massive Hg contamination is bound to unsaturated zone and decreased with depth. Hg concentration on the upper horizon of soils range on the order of tens to hundreds (n*10 to n*100) $mg.kg^{-1}$. Hg concentration on the depth of about 1.5 m below ground range on the order of 0.X to X.= $mg.kg^{-1}$. The higher concentrations are found to electrolysis and PVC Plants areas.

The last monitory field works were done during July and October 2004 from UT – LACH (Analytical Chemistry Section of University of Tirana). 61 surface soils were collected (15 cm deep from the surface level) for monitoring inside territory of the plant and in its periphery. The results are given in table 4.

In determining mercury in soils, the attention was focused in five Zones as is shown in figure 4. The area was divided in five zones: Zone I- The most contaminated site of Electrolysis Building and PVC Plant (deepest color in figure 4); Zone II – The contaminated site around Electrolysis Building and PVC Plant (higher color in figure 4), Zone III – The next contaminated site (yellow color in figure 4); Zone IV The less contaminated site (white color in figure 4) and Zone V – The territory outside the Plant. The area extent of contamination in individual depth levels is given in figure 9. These data will serve to investigate the actual situation of the area after intervention by some industrial activities on the area.

Table 4 Hg content in soil samples (mg/kg, DW)

	N	*Range of Hg concentration*	*X*	*Abnormal Values*
Zone 1	12	499.08 291845.9	46949.1	2 points with 300gr kg Hg
Zone 2	10	186.77 10155.6	1271	1 point with 685.38 mg kg Hg
Zone 3	13	10.27 408.3	71.4	2 points with 500 mg kg Hg
Zone 4	13	12.99 33.71	23.4	1 point with 455.61 mg kg Hg
Zone 5	13	0.041 3.21	0.398	

From the data listed in table 4, it is very clear demonstrated that the situation of Hg distribution in the contaminated area stand be the same as the studies performed in the past. Due to intervention in the area through some industrial activities, the Zone

IV is appeared less contaminated in Western part. The situation surround Electrolysis and PVC Plants, is different, too. Mercury content in area included in Zone 4 is also different. Two are the factors affected: the erosion and human activity.

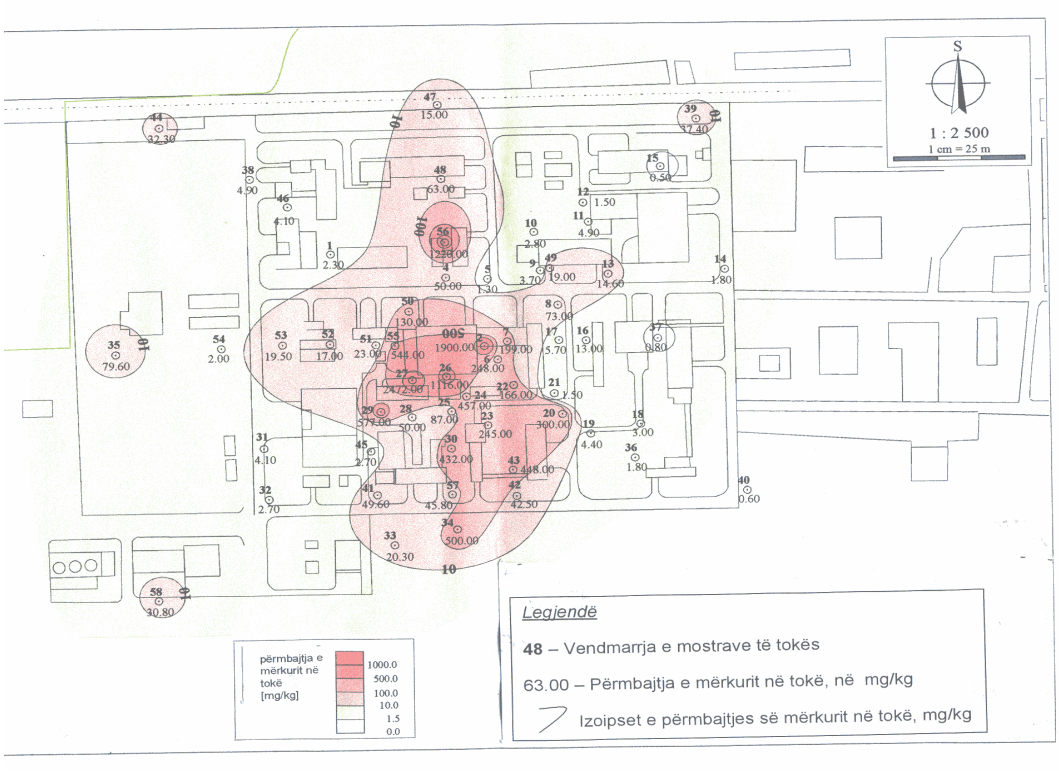
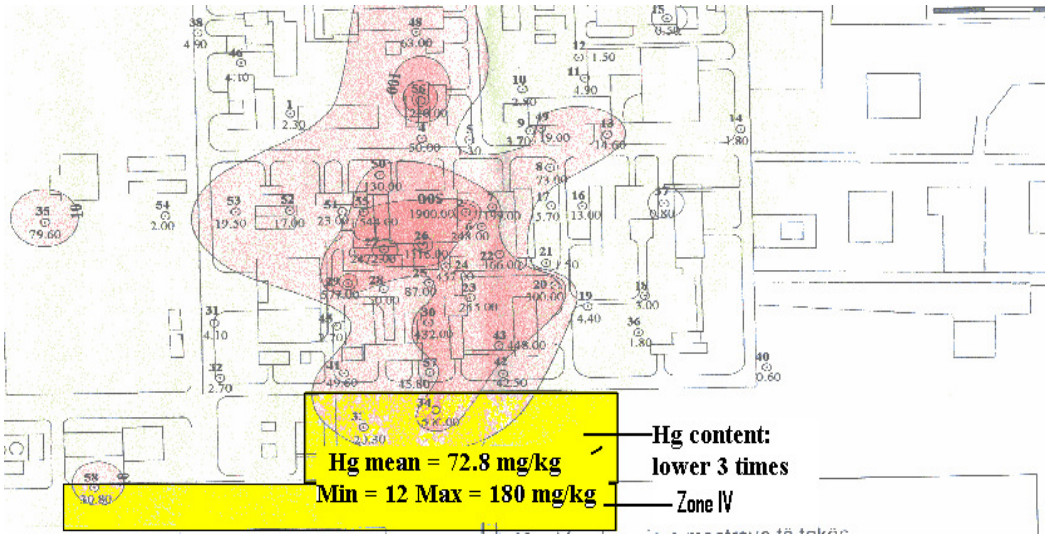


Figure 9 The map of Hg distribution

(a) Erosion (b) human activity

Figure10 Views of the area

The contaminated soils of Zone IV are moved around Electrolysis and PVC Plant



(a) East part of the Plant *(b) North part of the Plant*

Figure 11 Some views o the territory of the factory after the transport of the soils

Due to the transport of the soils to these areas, the soils are also very contaminated in 1.5 m deep, too. It is clearly demonstrated through the analysis of five soil samples positioned in the area of PVC and Electrysis Plants were collected in three different depths (0.20, 0.75 and 1.5 m). The results of the analysis are given in histograms of figure 12.

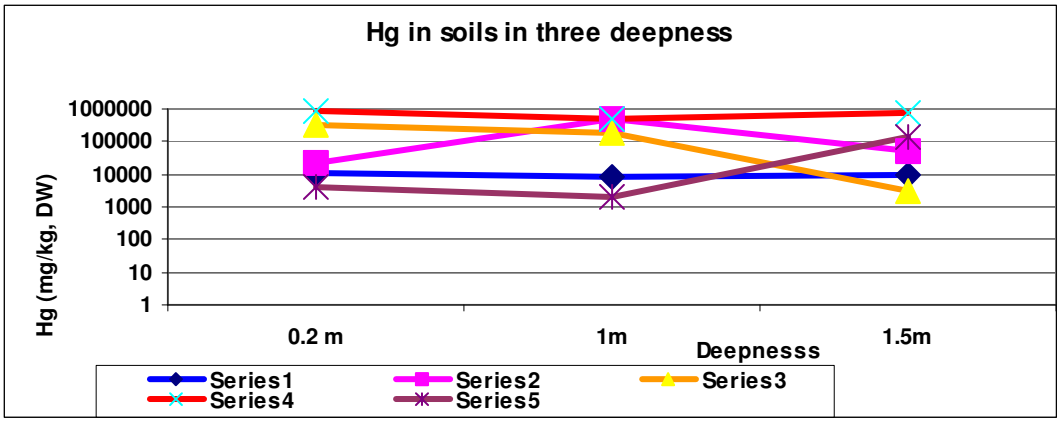


Figure 12 The histograms of Hg content of soils collected in three different deeps

10 surface soil samples were collected in two parallel lines with seashore in North direction outside of the plant. The samples were collected 200 - 300 m far from each other (July, 2003). The first group of the samples was collected about 150 m far from the end of plant. The samples were analyzed by CVAAS method and the results are listed in table 5.

Table 5 Hg content in soil samples outside the plant (in mg/kg, dw)

No.	*1*	*2*	*3*	*4*	*5*
Line 1	0.098	0.071	0.046	0.11	0.20
Distance from the plant (m)	150	400	700	1000	1300
Line 2	0.064	0.043	0.042	0.11	0.18
Distance from the plant (m)	150	400	700	1000	1300

The analyzed samples present Hg concentrations less than 20 mg/kg (the limit of polluted samples in Great Britain), but they show concentrations inside the range of 0.07-0.3 mg/kg, which is "preliminary critical limits to prevent ecological effects" according UNEP Chemicals[12]. The content of Hg was decreased as the distance from the plant and from the seashore was increased (No. 1 to 3). Due to higher content of organic matter in last four samples (No 4 and 5) higher content of Hg was found compare to other stations.

The content of Hg was decreased as the distance from the plant and from the seashore was increased (No. 1 to 3). Due to higher content of organic matter in last four samples (No 4 and 5) higher content of Hg was found compare to other stations. The results o mercury concentration of our surface samples were some time higher than background level [5], so special normalization procedures are necessary to allow this assessment of anthropogenic and natural contaminants in soils. Geo-accumulation index I_{geo} ($I_{geo} = \log_2 \frac{C_n}{1.5B_n}$, where C_n represents elements estimated concentration level and B_n represents elements background level, (B_n=0.04 mg/kg, dw) was calculated for all soil samples. The results are listed in table 6.

Table 6: Geoaccumulation index I_{geo} of sediments samples of Vlora Bay

Element	*Mean value of I_{geo}*	*Min-Max*
Hg	0.37	0.042 – 0.200

Geo-accumulation index I_{geo} *of* mean concentration of mercury in these soils resulted 0.28, showing that levels of Hg in this area are near the normal values[2].

4.1.2. Mercury concentration in soil air

Mercury concentrations in soil air were conducted in the same network of points as the measurements of Hg in air (t=26 – 42^0 C). The concentrations of Hg vapors were plotted (see figure 13).

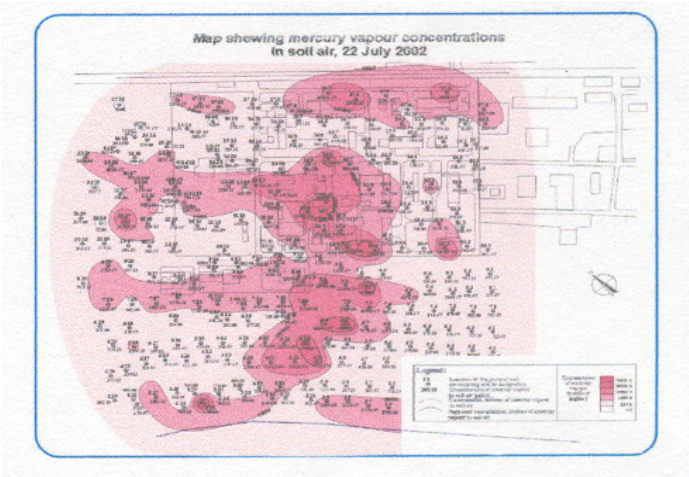


Figure 13 Map of concentrations of Hg vapors in soil air

From the given map there is evident an area with high Hg concentrations (Hg concentration goes up to 30 mg.m^{-3}), which is near the electrolysis building. This area is extended in the NW-SE direction. The second area with Hg concentration also up to 30 mg.m^{-3} is found by the road to the site boundary. Anomalies of lesser extent in terms of their area were found in the proximity to the NW from the anomaly of the electrolysis building and by the PVC-SODA-Zvernec road, where the Hg concentration reached 36, 000 ng.m^{-3}. In the area of sludge depositary, there was detected an anomaly extending in W direction, where the Hg concentration reached 50, 000 ng.m^{-3}. This anomaly also runs into a part of the area of the demercurisation station building.

4.2. Mercury concentration in air

Mercury concentrations in air were determined in two different height level; 0.15 m (t=26 – 42^0 C) and 0.1 m above ground. 662 measurements were performed in 331 measurement points. The concentrations of Hg vapors were plotted (see figure 14).

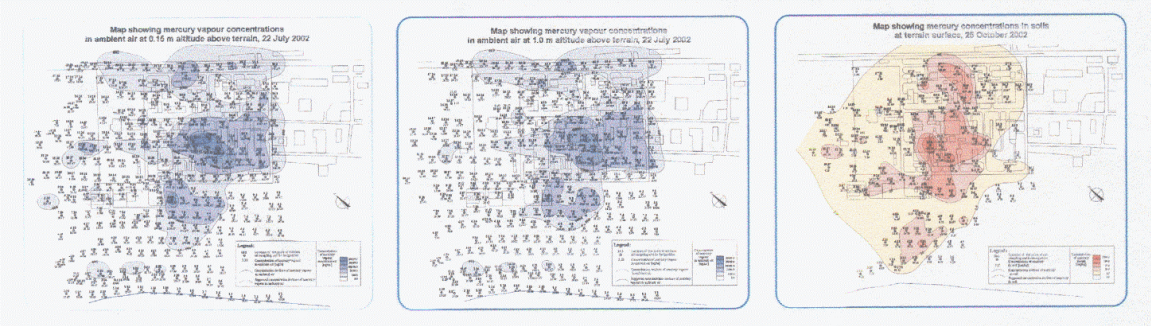


Figure 14 Map of concentrations of Hg vapors in air

From the given map there is evident an area with high Hg concentrations (Hg concentration goes to 30 $mg.m^{-3}$), which is near the electrolysis building. This area is extended in the NW-SE direction. The second area with Hg concentration to 25 $mg.m^{-3}$ is near the demercurization station building. Anomalies of lesser extent in terms of their area were found in the proximity to the NW from the anomaly of the electrolysis building and by the PVC-SODA-Zvernec road, where the Hg concentration reached 3, 768 $ng.m^{-3}$. The measurements of mercury concentrations in the air at a height of 1.0 m from the ground, confirmed the anomalies existing near the electrolysis building (the Hg concentration fluctuated above 20, 000 $ng.m^{-3}$); the anomalies existing near the demercurization station building (the Hg concentration fluctuated above 1, 000 $ng.m^{-3}$) and in the proximity to the NW from the anomaly of the electrolysis building and by the PVC-SODA-Zvernec road (the Hg concentration fluctuated above 1, 857 $ng.m^{-3}$).

4.3. Mercury concentration in groundwater samples

Groundwater samples were taken in the static state of the water-bearing layer. The quality of groundwater in the area concern is very variable. The pH values fluctuated from basic to neutral character (see table 7).

Table 7 Physical-chemical parameters of groundwater (sampling-23.07.2002)

	M-1	*M – 2*	*HM - 1*	*HM – 2*	*HM - 3*	*HM - 4*	*HM -5*
pH	*8.1*	*8.1*	*7.3*	*11.1*	*11.8*	*7.4*	*7.4*
K($\mu s.cm^{-1}$)	*52,100*	*52,000*	*2,510*	*13,760*	*6,520*	*1,978*	*785*
Hg [$\mu g.l^{-1}$]	*<1.0*	*<1.0*	*2.80*	*<1.0*	*47.0*	*<1.0*	*<1.0*

Criterion C for mercury is exceeded in lime sludge depositary. The relative abundance of main groups of ions of seawater and groundwater is displayed in a triangular diagram (see figure 15).

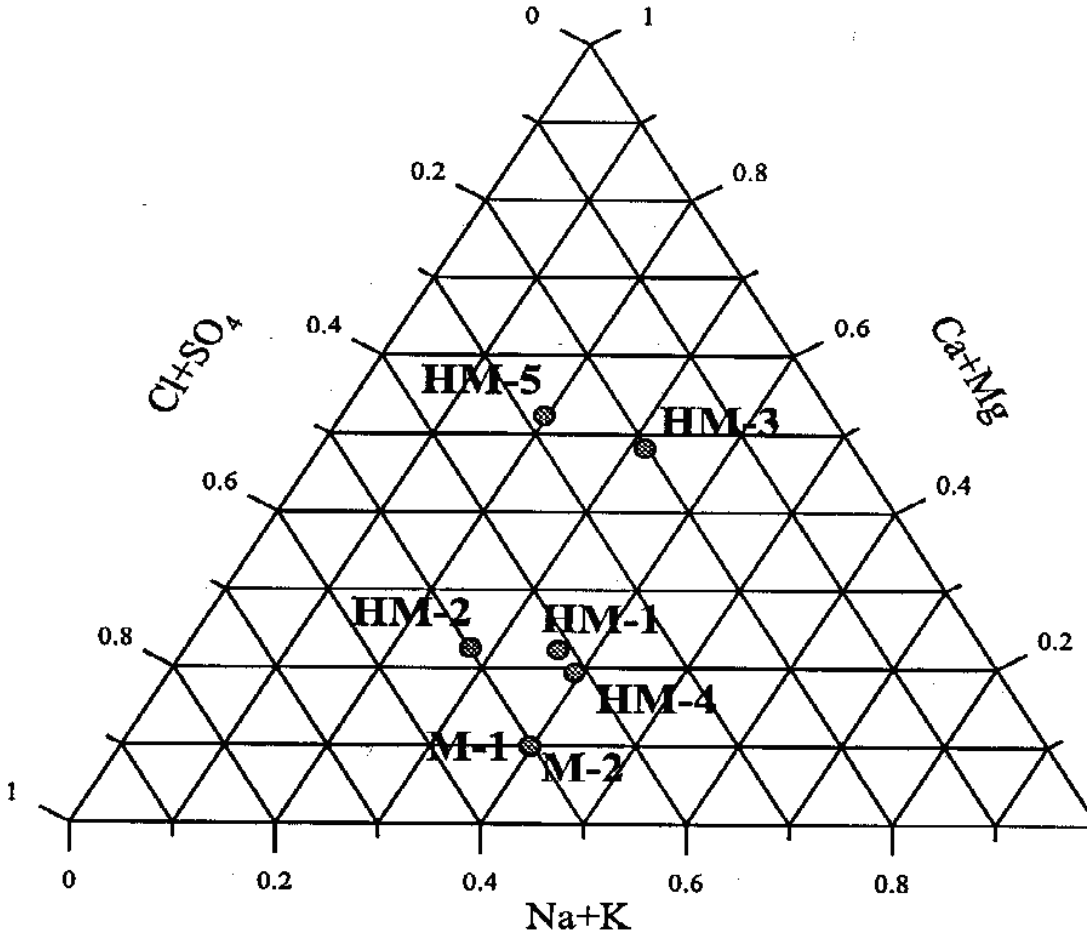


Figure 15 The relative abundance of main groups of ions of seawater and groundwater

The graph presents the ratio of (Na+K):(Ca+Mg):(Cl+SO_4) expressed in percents of the sum of equivalent concentrations. Due to carbonates property of the area[20], HM-3 and HM-5 water samples strikingly differ from the other water samples by their relative abundance of main groups of ions, namely by their higher percentage abundance of (Ca+Mg) group.

4.4. The effect of Mercury to the people living inside territory of Vlora Hot Spot

Some statistical results for mercury content in hair samples for all the subjects in the study are shown in table 9 and are illustrated in figures 16 and 17.

*Table 8 Hg content in two different groups of un-exposure people living in Tirana**

Index	*N (People)*	*Mean, (μg/g)*	*Mediana (μg/g)*	*Min (μg/g)*	*Max (μg/g)*
6th Group (age: 4-5 years)	37	0.398	0.267	0.25	1.601
7thGroup (Age:22-23 years)	24	0.405	0.395	0.195	1.698

** The analysis were performed on September 1998*

Table 9 Hg content in different groups of exposure people in Vlora Hot Spot

Index		*N (People)*	*Mean, (μg/g)*	*Mediana (μg/g)*	*Min (μg/g)*	*Max (μg/g)*
TOTAL		72	0.806	0.698	0.216	1.953
1st (People)	*F*	36	0.817	0.713	0.216	1.622
(age: 2-70 years)	*M*	36	0.798	0.685	0.256	1.953
TOTAL		36	0.855	0.705	0.256	1.953
2nd (Children)	*F*	16	0.903	0.705	0.452	1.622
(Age:2-12 years)	*M*	20	0.817	0.708	0.256	1.953
TOTAL		9	0.788	0.596	0.216	1.953
3d (Yong)	*F*	5	0.751	0.576	0.216	1.345
(Age:13-25)	*M*	4	0.826	0.615	0.382	1.953
TOTAL		*18*	0.677	0.691	0.270	1.344
4th (Middle)	*F*	*10*	0.688	0.747	0.270	1.066
(Age:25-40)	*M*	*8*	0.676	0.685	0.422	1.344
TOTAL		9	0.891	0.853	0.422	1.712
5th (>45 years)	*F*	5	0.872	0.853	0.520	1.356
	M	4	0.915	0.762	0.422	1.712

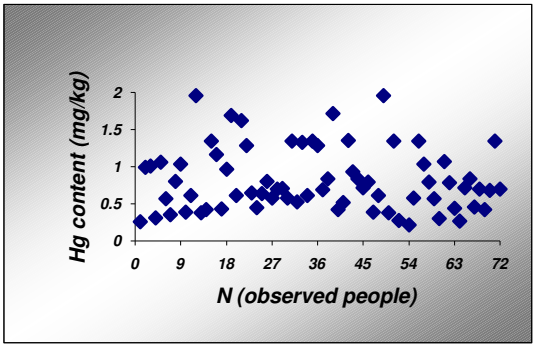


Figure 16 Hg content in observed subject (N=72) different groups of exposure(N=72)

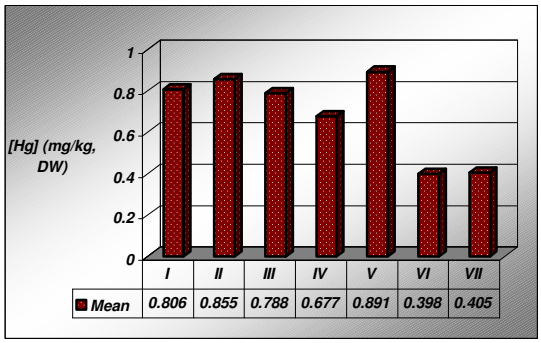


Figure 17 The diagram of Hg distribution in and un- exposure (N=61) people

The overall mean of mercury content in hair samples of exposure people (0.806 μg/g) was bellow the range of 1-2 μg/g decided by WHO [29] as normal range for the population which does not consume fish with high methyl mercury content. The highest value found (1.953 μg/g) is within this interval, too, but compare with overall mean of mercury content in hair samples of un-exposure people (0.402 μg/g) the so mentioned values of exposure people are two times higher. The most critical group is the second group, the children 2-12 years old, (N=37), where 75% of them belong to the range up to 0.5 μg/g (33% of them belongs to the range 1-2 μg/g and about 42% of them belong to the range 0.5-1 μg/g, see table 10 and figure 18). The reference concentration for exposure healthy controls of Hg non-essential, toxic trace elements in body tissues and fluids is about 6 ng/ml [30], or converted to hair samples ($Hg_{Blood/Hair}$ =1:250 [31, 32, 33, 34]) it should be about 1.5 μg/g. Based on this criteria the group of exposure children should be under healthy controls.

As it is shown from table 9 and figure 18, a significant difference exist on mercury content between exposure and un-exposure people. About 70 to 90% of the subjects from exposure people belong to the highest range of Hg content found for exposure people (Hg content 0.5-2 μg/g), except the third group, where about 55% of the peoples belong to the lower range of mercury content (0.35 to 1 μg/g). In contrary,

about 85 to 90% of the subjects from un-exposure people belong to the lowest range of Hg content found for these group of people (Hg content <0.5 μg/g.

Table 10 The % of people with different range of Hg content

Hg range (μg/g)	*0.1-0.35*	*0.35-0.5*	*0.5-1*	*1-2*
1st Group (N=72)	11.1%	18.1%	43%	27.8%
2nd Group (N=37)	13.9%	11.1%	41.7%	33.3%
3d Group (N=9)	11.1%	33.3%	22.2%	33.3%
4th Group (N=18)	11.1%	22.2%	50%	16.7%
5th Group (N=9	-	11.1%	66.7%	22.2%
6th Group (N=37)	59.5%	35.1%	5.4%	8.3%
7th Group (N=24)	51.4%	33.7%	6.6 %	-

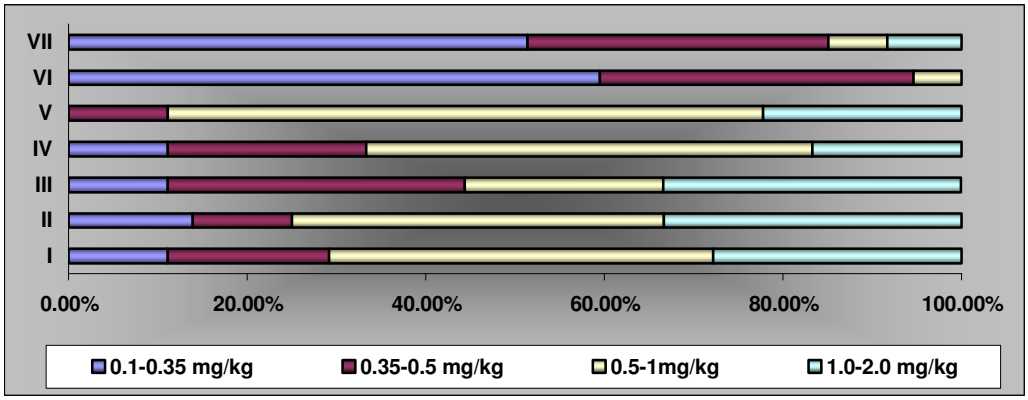


Figure 18 The histogram of the number of subjects (in % against the number of people within a certain group) belong to different Hg content range

Linear correlation coefficients between Hg content and various parameters, such as exposure time, age, frequency of fish consuming were calculated to identify the relationship between them, as well as the dependency of Hg content from the sex of the subjects under investigation. No any significant r-values were found between Hg content and the parameters mentioned above.

CHAPTER 5: THE IMPACT OF "VLORA HOT SPOT POLLUTION" DIRECTLY IN ADRIATIC SEA

5.1. Mercury concentration in sediment samples

Results of a systematic study of the sea area near Soda-PVC plant are presented in table 5[3,4]. The sea floor sediments samples (5-10 cm depth) were collected along five axes in both sides of plant, at three distances of shore: 100, 300 and 700 meters (see figure 19). The results are listed in table 11 and are illustrated in figure 20.

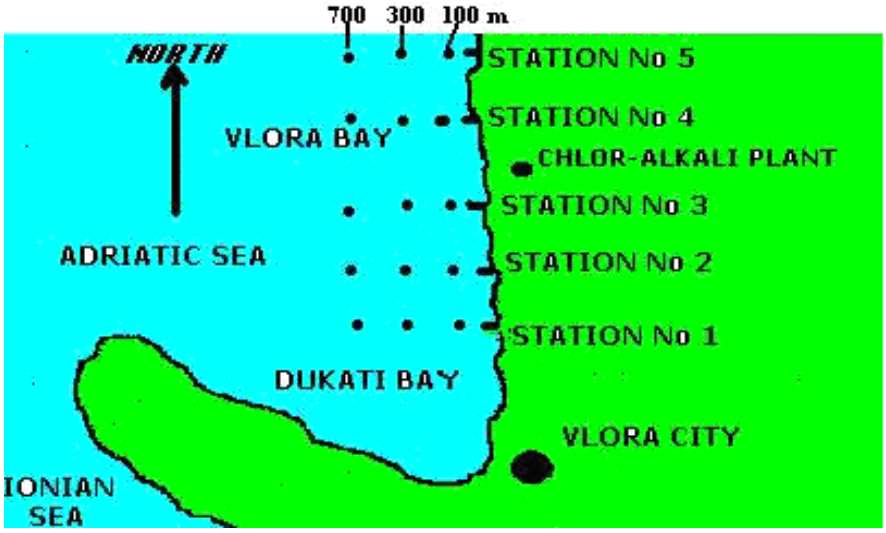
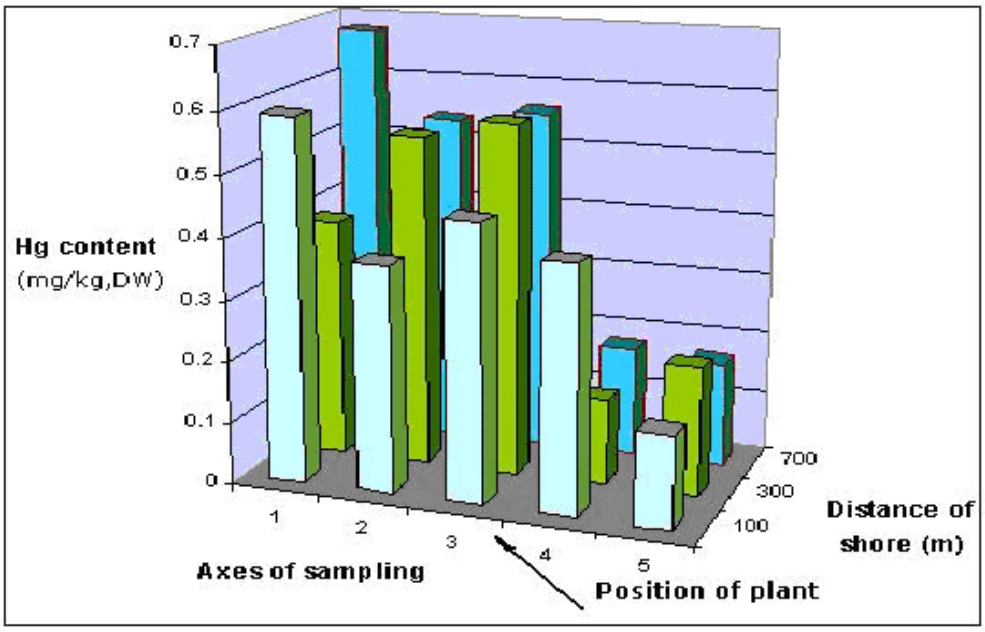


Figure 19 The map of sampling position (marine sediments in the area near Soda-PVC plant)

Table 11. *Concentrations of Hg in marine sediments in the area near Soda-PVC plant (in mg/kg DW)*

Distance from shore, m	Axis 1	Axis 2	Axis 3	Axis 4	Axis 5
100	0.59	0.37	0.45	0.40	0.15
300	0.39	0.54	0.57	0.14	0.21
700	0.68	0.54	0.56	0.18	0.17



(a)

(b)

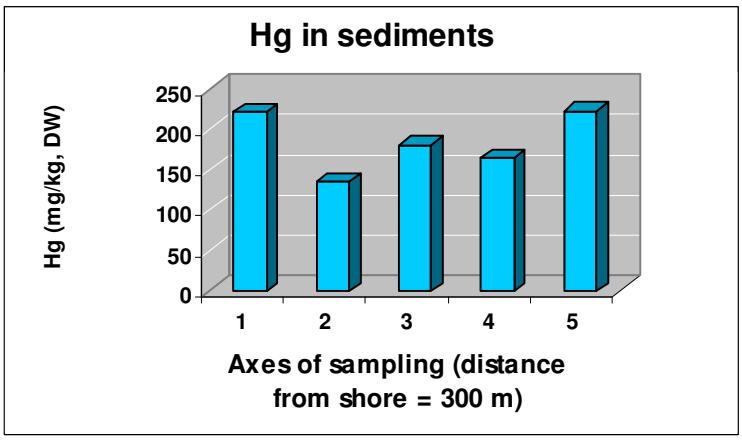


Figure 20 The diagram of Hg distribution in different stations (marine sediments in the area near Soda-PVC plant) (a) sampling time: 1994 (b) sampling time: October, 2004

Spatial distribution of Hg in the studied area shows that the most polluted zone is not restricted to the very vicinity of the PVC plant (axis III and IV). A tendency of relocation of the pollution to the west-southern part of the Bay (axis I and II) is observed, probably due the hydrological flows. It was found that the fine size fraction of sediment accumulates the major part of Hg and thus is the most important accumulator and carrier of Hg in this area. Average concentration of Hg in the fraction less than 63 μm is 0.60 mg/kg, whereas in the fraction 60-250 μm it is only 0.23 mg/kg.

From above results it could be seen that Hg levels in Vlora samples are much higher than levels of other Albanian seacoast areas (0.040-0.120 mg/kg)[5, 14], and Southern Adriatic Sea (0.020-0.070 mg/kg)[11]. They are at the same level as those of polluted sediments of Northern Adriatic Sea[10,11].

Some normalization procedures may be used for grain size normalization, aiming to separate anthropogenic and natural contaminants in sediments, particularly of inorganic pollutants. Geoaccumulation index I_{geo} ($I_{geo} = \log_2 \frac{C_n}{1.5B_n}$, where C_n represents elements estimated concentration level and B_n represents elements background level) is calculated for all sediment samples. The results are listed in table 12.

Table 12: Geoaccumulation index I_{geo} of sediments samples of Vlora Bay

Element	*Mean value of I_{geo}*	*Min-Max*
Hg	3.88	2.52 – 4.75

Geoaccumulation index I_{geo} for mean concentration of mercury in sediments of Vlora Bay, resulted 3.88, showing that levels of Hg in sediments of Vlora Bay (marine sediments in the area near Soda-PVC plant) are 22 times higher than normal values[2], so anthropogenic contamination by Hg in sediments of this area exist.

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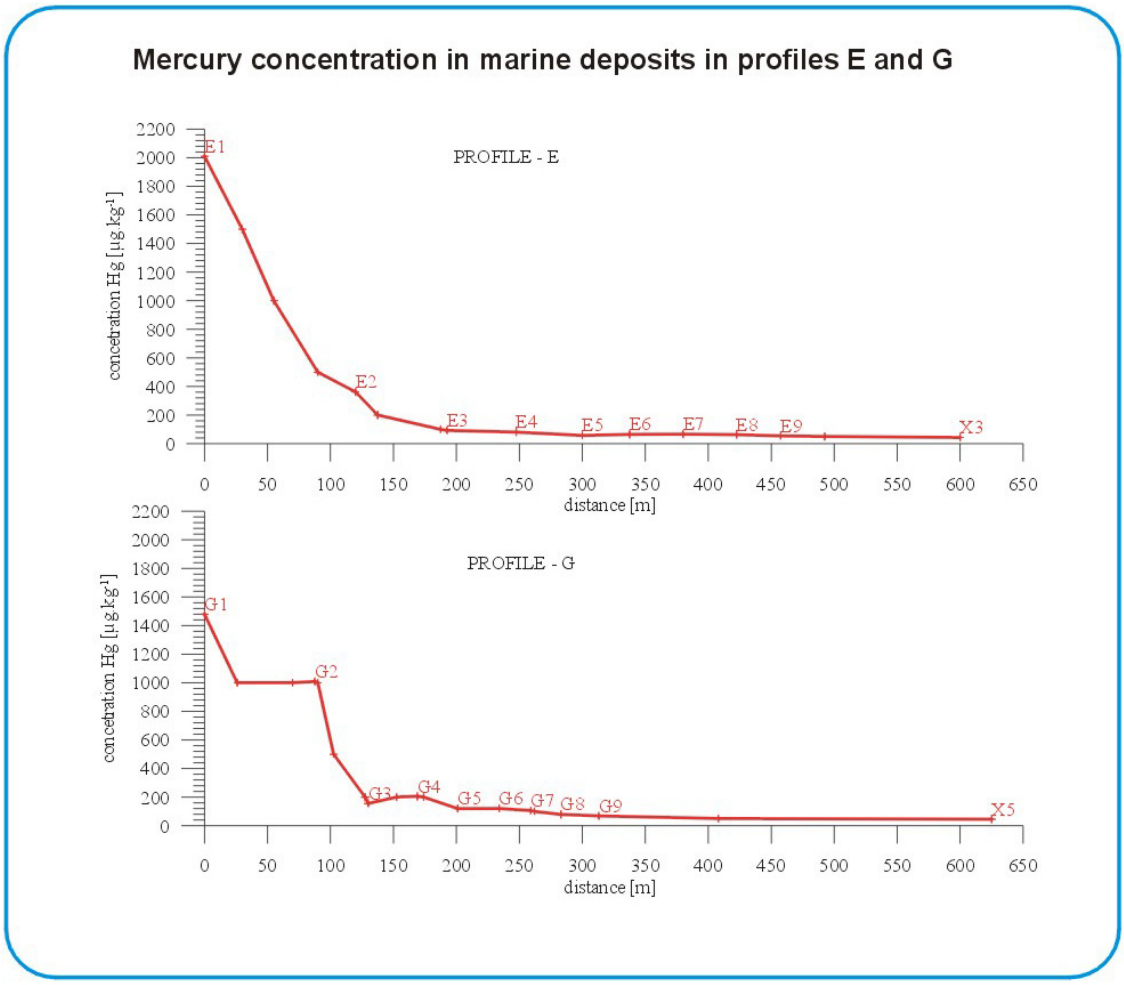


Figure 21 Hg concentration in marine deposits (profiles E and G)

A rapid drop in Hg concentration with the increasing distance from the shoreline exists. The marked drop is evident approximately to a distance of 300 m from the shore. The highest Hg concentration were found in points E1 (2,010 µg.kg^{-1}) and F1 (1,933 µg.kg^{-1}), which are situated in the proximity of the sewerage outlet from the PVC-SODA factory. The course of Hg concentration on the shoreline (d=0 m) is given in figure 20, where also the position of sewerage outlet is displayed.

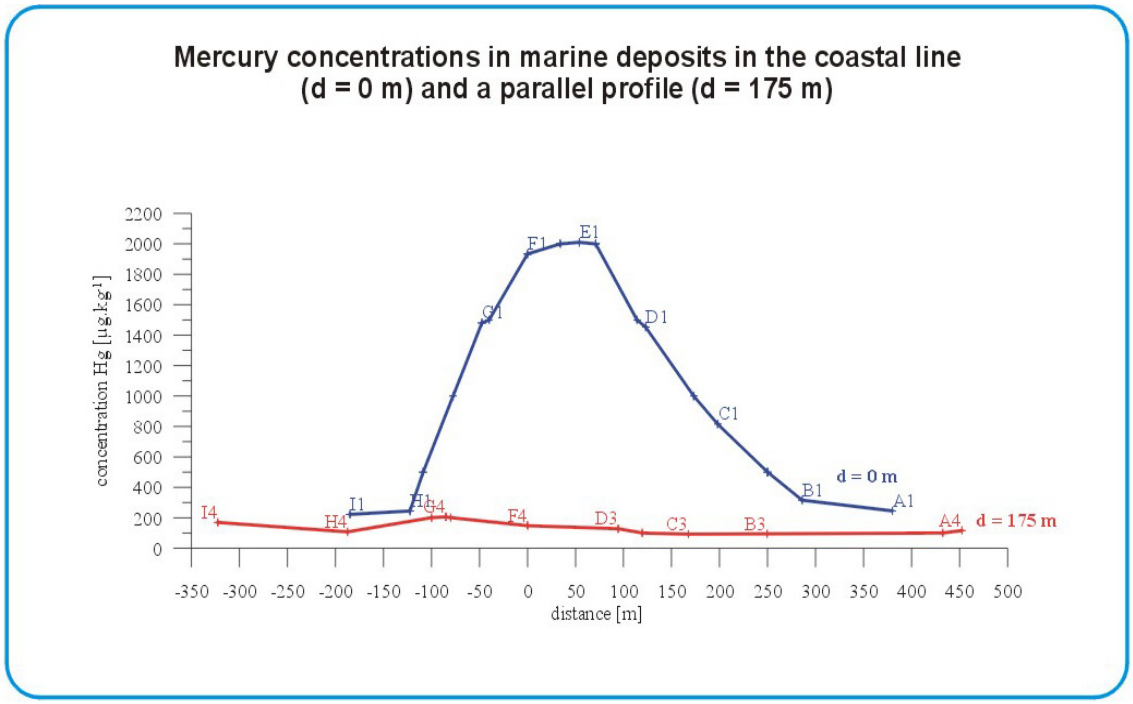


Figure 22 The Hg concentration in deposits at a distance d=175 m from the shore (the graph by the line d=175 m)

Hg concentration decreased in two directions: parallel to shore line and in the direction perpendicular to the detected maximum.

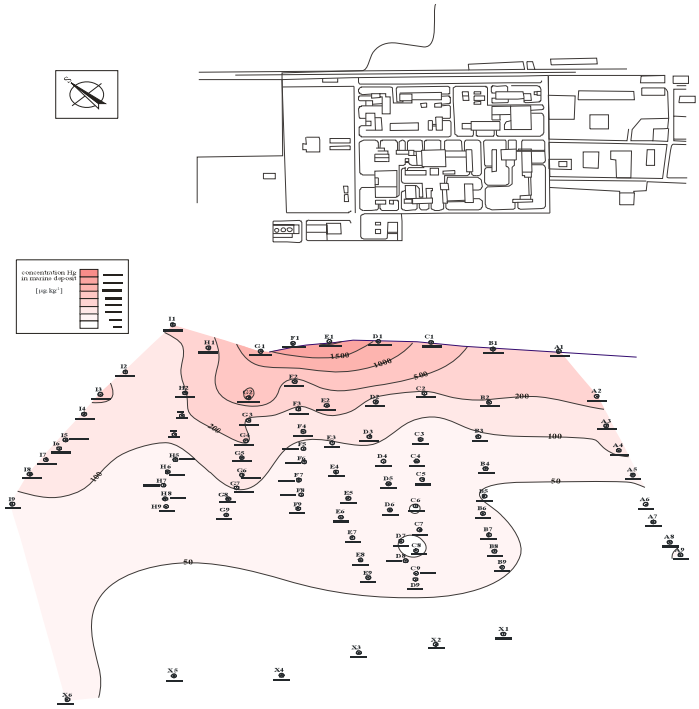


Figure 23 The map of Hg distribution in marine deposits

Compare with previous monitory studies, the content of tot. Hg in seawater samples appeared to be in the same level (110-140 ng*ml-1). It means that Hg pollution in Vlora Bay, remain to be problem for a long time in the future (Vlora Bay is a half closed Bay). The content of MeHg in seawater samples is about 15% higher than before, so methylation process is present. The situation of Hg content in sediments is similar with our last investigations (1998). The station near Soda-PVC is the most contaminated. The level of Hg concentration is the same. May be it related with the transport of contaminated soils from seaside to other places.

5.2. Mercury concentration in seawater samples (Total, Inorganic And Organic Mercury)

Seawater samples in contact with bottom sediments were collected in the same profile as the marine deposits (see figure 17 and 18). Seawater samples were collected at a level of about 0.15 m above the bottom of the sea. The samples were fixed with HNO_3. The higher Hg concentration were found at a shoreline between points G1 to G1, with the highest concentration of 3.35 $\mu g.l^{-1}$ found in point G1 (see figure 17).
Results of total and organic mercury in seawater samples collected in five Adriatic stations are presented in table 114 [7, 14, 15, 16].

Table14. Concentrations of mercury in seawater of Vlora Bay and Durrës Bay (station No. 1 and 5 are in polluted areas)

No.	*CONCENTRATION OF MERCURY (in µg/L)*			
	Station	*Inorganic Hg*	*Organic Hg*	*Total Hg*
1	Vlora, near PVC plant	0.061	0.060	0.121
2	Vlora, "Uji i Ftohtë"	0.043	0.053	0.096
3	Durrës, "Currilat"	0.037	0.060	0.097
4	Durrës, "Golem"	0.036	0.044	0.080
5	Durrës, "Porto Romano"	0.039	0.063	0.102

The highest Hg concentration values were found in Vlora , near PVC plant. The percentage of organic mercury to total mercury in water varies from 50 to 62 %.

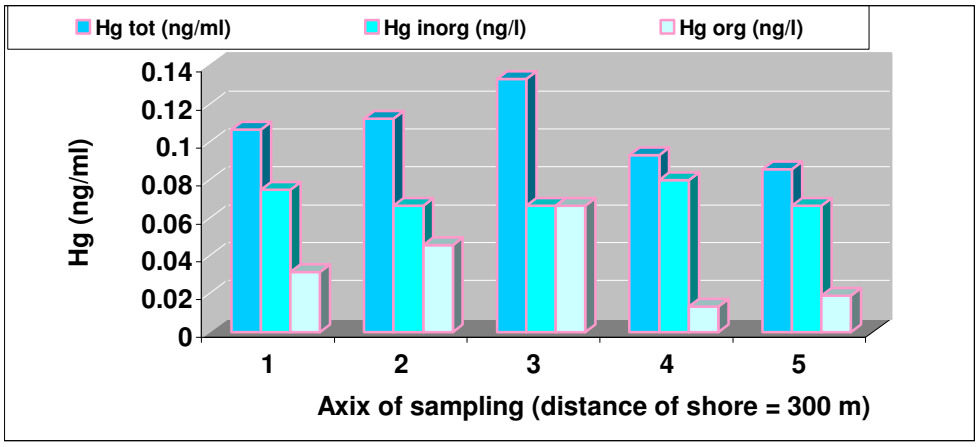


Figure 24 Hg content in seawater samples (in ng/ml) (samping time: October, 2004)

Concentration of inorganic Hg in water samples taken in the vicinity of PVC plant is about 1.6 times higher than in the other samples. All samples analyzed contain total

Hg concentration exceeding the 12 ng/L, level recommended by USEPA to protect against chronic effects to aquatic wildlife.

5.3. Mercury concentration in biota samples

Levels of mercury content in mussels (*Mythilus galloprovincialis*) in some of Albanian seacoast areas are shown in figure 12[9, 2, 15]. Notably higher Hg levels are found in macroalgae species in one contaminated site near plant in comparison with one reference site about 25 km far[6]. Monitoring of heavy metals, including mercury, in algae's samples, is important evaluating environmental situation of aquatic systems. Accumulating of heavy metals/or mercury from aquatic biota, is a suitable tool for the monitory of average load. Results for both sites are presented in the table 15.

Table 15. Mercury concentrations (min-max) in macroalgae samples (in μg/kg DW)

Sampling site	Algae species		
	Cladophora sp. (Clorophyceae)	*Enteromorpha sp. (Clorophyceae)*	*Liagora sp. (Rhodophyceae)*
Near PVC plant ("Porti")	230 – 297	155 – 235	222 – 230
Remote area ("Orikum")	97.3 - 103	90 - 102	131 – 140

Due to the fact that some of macro algae species are able to accumulate heavy metals in their tissues and some others, not, sometimes it seems to be difficulty in finding any relation between heavy metals content in water-algae system. If we compare the content of Hg between the same species of Vlora Bay and Dukati Bay (Orikumi Station, chosen as background level) it is clearly demonstrated the Hg content of the species of Vlora Bay is 2.5 to 3 times higher than Dukati Bay or 6 times higher than Saranda area.

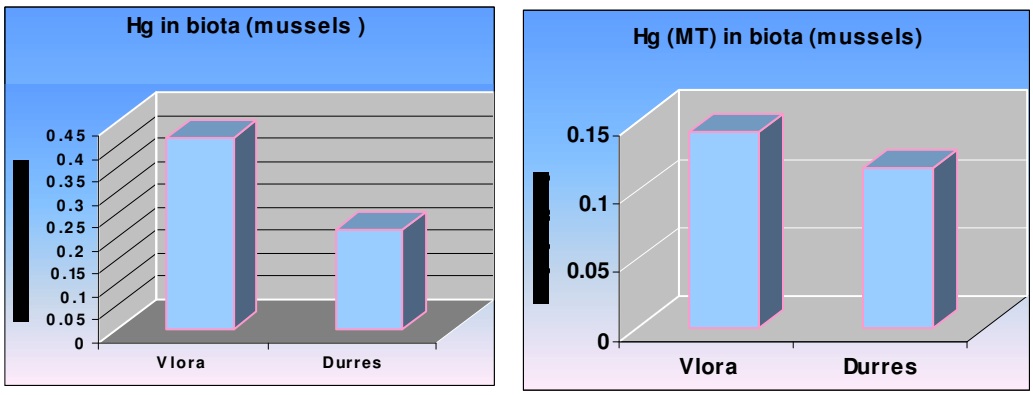


Figure 25 Hg concentration in biota samples (a) total Hg, (b) Metalthionine

Compare with previous monitory studies, the content of tot. Hg in biota samples appeared to be about three times higher than the year 1998. It is about two times higher than the samples collected in Durres Bay. It means that Hg pollution in Vlora Bay, remain to be problem for a long time in the future (Vlora Bay is a half closed Bay)

Chapter 6: The impact of "Vlora Hot Spot Pollution" around Vlora Bay

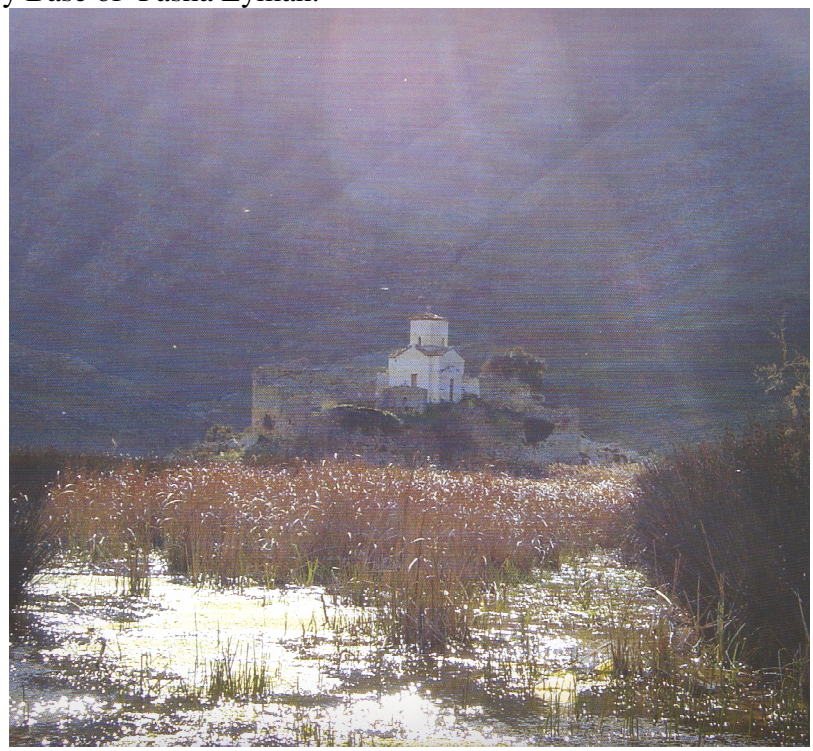
6.1. The concentration of mercury in seawater, sediments, biota and plant samples

Vlora Bay presents the natural boundary between the Adriatic Sea and the Ionian Sea and has a wonderful view and beach. Vlora Bay presents an important source of touristy not only for Vlora area, but also for Albania. Some important beaches and two important Lagoons, Narta and Orikumi Lagoons, National Park of Llogora, positioned in this area, so the examination of trend of mercury pollution of the area is very important.

View from National Park of Llogora

Narta Lagoon positioned on 40°30'N and 19°18'E. It is a part of Vlora Myzeqe area just in South part of the delta of Vjosa River. It is the biggest and most important Lagoon in Albania. Its area is about 45 km^2. There is a littoral aluvional narrow belt, which separate the Lagoon from the Sea. The North part of the Lagoon, about 1/3 of its total area, is used as saline for many years. The deepness of Lagoon varied from 0.3 to 1 meter.

Orikumi Lagoon is positioned in Dukati Bay, South part of Vlora Bay, just in natural border between Adriatic and Ionian Sea (40°30' N and 19°18' E). Its total area is about 150 ha, with maximal depth of about 3 m.
Orikumi area positioned very near National Park of Llogara (1010 ha), mentioned for its touristy views, for its very rich fauna and flora. The area from Vlora to Orikumi is famous for its preferable beaches. The main activity of this area is the Marine-Military Base of Pasha Lyman.



The ruins of ancient Orikumi city are just inside Lagoon. The ancient Orikumi city participated in Taulant's state and was build up nearly at the VIth century before our eras. From ancient time till now, the port of Orikumi was an important military and commercially port. Orikumi port was mentioned during the fights between the 5th Philip of Macedonia and Roma. It was mentioned too, during the fights of Jul Cesar against Pompous. Orikumi was destroyed after a strong earthquake at 2nd century before our era. The ruins of Orikumi are just in Lagoon.

Mercury concentration in various environmental samples has been monitored for the assessment of the mercury levels, especially concerning pollution problems in Vlora Bay. The main source of mercury contamination in Vlora Bay is metallic mercury. As it is described in Chapter 5 Hg concentration in sediment samples decreased in two directions: Parallel to shore line and in the direction perpendicular to the detected maximum.

For the evaluation of mercury pollution in Vlora Bay, some of our previous studies are listed bellow. The investigation was carried out in 18 stations (6 in Narta Lagoon, 5 in Orikumi Lagoon and 7 in open sea, 300 m far from the shore were chosen).

The positions of sampling sites and monitory station are shown in figure 26.

Station No 1: N 40° 30' 217'', E 019° 27' 070'', positioned near the sewages disharge chanal comming from the collector of Vlora city.

Station No 2: N 40° 32.246', E 019° 24.100', positioned near Big Dajlan.

Station No 3: N 40° 31.329', E 019° 23.966', positioned near Small Dajlan.

Station No 4: N 40° 30.444', E 019° 26.120', positioned near the area of the dumps from ex-chlor alkali plant.

Station No 5: N 40° 31.128', E 019° 27.145', positioned near the drainage canal of Panaja field, as well as near the hills of Bestrova and Kerkova.

Station No 6: N 40° 30.767', E 019° 27.085', positioned near positioned near drainage canals of Panaja field, as well as near the hills of Bestrova and Kerkova. The canal of sewages of new buildings constructed after the year 1990, positioned here.

Station No 7: N 40° 32.646', E 019° 24.387', positioned in sea, near Small Dajlan (reference station).

Station No 13: N 40° 19.329', E 019° 26.237': Positioned in Sea; the communication part between Orikumi Lagoon and the sea.

Station No 8: Positioned 300 m far from the shore in PVC Plant

Station No 9: Positioned 300 m far from the shore in "Kampi I Pionierve"

Station No 10: Positioned 300 m far from the shore in Jonufra site

Station No 11: Positioned 300 m far from the shore in Radhima site

Station No 12: Positioned 300 m far from the shore in Orikumi town

Station No 14: N 40° 19.198', E 019° 26.555': Positioned near the communication canal between Lagoon and Sea.

Station No 15: N 40° 18.846', E 019° 26' 324': Positioned in South part of Lagoon. There was a seawall surround this area constructed on 1965, after the irrigation of Dukati field. Close to irrigator pass the main drainage canal of Dukati Field, so the infiltrations from the canal to Lagoon may be present.

Station No 16: N 40° 18.735', E 019° 26.149': positioned on Southwest part of the Lagoon. There are some discharges of underground water coming from Marmiroi Church, about 500 m far from Lagoon. This water coming from Karaburuni Mountain has the characteristics of drinking water.

Station No 17: N 40°19.090', E 019° 25.954': Positioned in West part of Lagoon. The sewages of Military Base of Pasha-Lyman, discharged in this area.

Station No 18: N 40° 19.226', E 019° 26.251': Positioned near the communication canal between Lagoon and Sea.

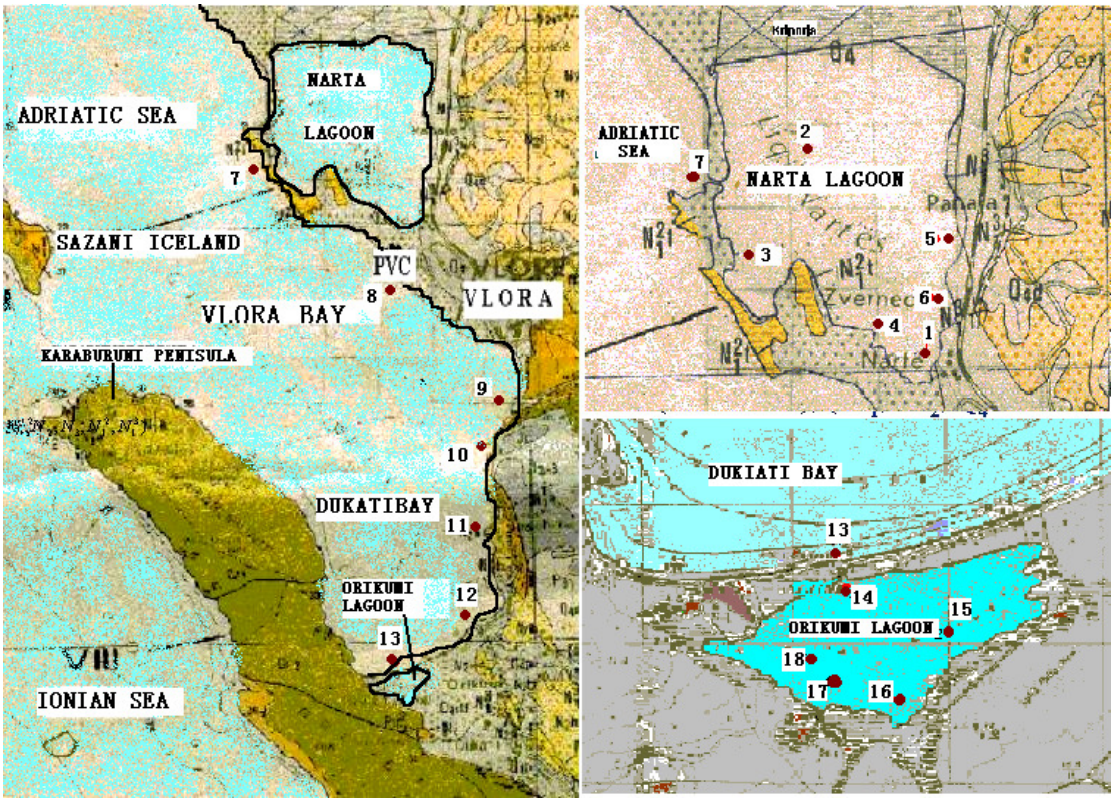


Figure 26 The map of sampling sites in Vlora Bay

(a)

(b)

Figure 27 Some views from (a) Narta and (b) Orikumi Lagoons

6.1.1. The concentration of Hg in seawater samples

The concentration of mercury in seawater samples are given in tables bellow.

Table 16. The concentration of Hg in seawater samples of Vlora Bay (ng/ml)

	Station						
Element	*7*	*8*	*9*	*10*	*11*	*12*	*13*
Hg	0.105	0□121	0□096	0.073	0.109	0.088	0.085

Table 17 The concentration of Hg in seawater samples of Narta Lagoon (ng/ml)

	Station						
Element	*1*	*2*	*3*	*4*	*5*	*6*	*7 (Ref. St.)*
Hg	0.182	0.136	0.151	0.206	0.127	0.112	0.105

Table 18 The concentration of Hg in seawater samples of Orikumi Lagoon□ ng/m□

	Station					
Element	*14*	*15*	*16*	*17*	*18*	*13 (Ref. St.)*
Hg	0.108	0.126	0.078	0.096	0.114	0.085

Table 19. Some statistical data about the concentration of Hg in seawater samples of Narta and Orikumi Lagoons (ng/ml)

Lagoon	*Hg*			*Reference samples on Sea*	*The Class of Quality(NIVA Classification) [35]*
	Mean	*Min.*	*Max.*		
Narta	0.136	0.112 (6)	0.206 (4)	0.105 (7)	4th Class
Orikumi	0.102	0.078 (16)	0.126 (15)	0.085 (13)	3rd Class
Vlora Bay	0.096	0.073	0.121	0.080(Durres Golem)	

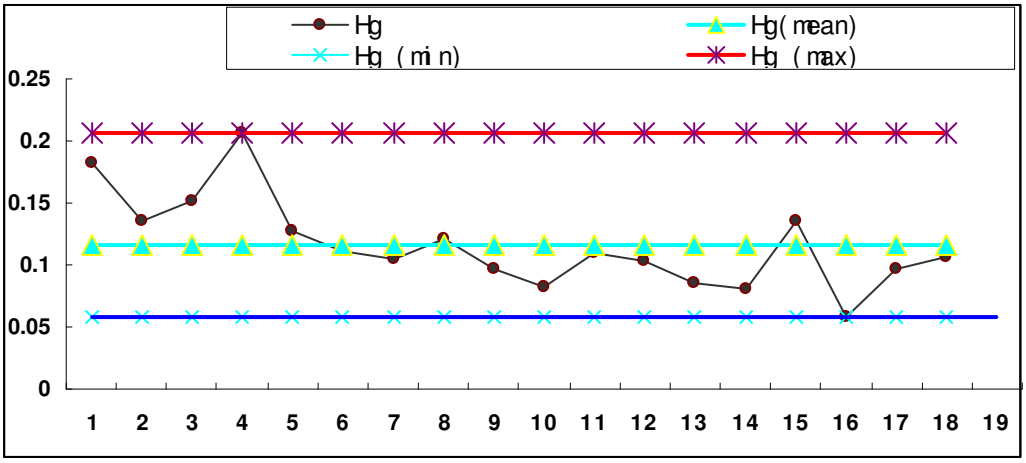


Figure 28 The histogram of Hg distribution in seawater samples (ng/ml)

Due to metallic form of mercury pollution and its very small soluble ability, the concentration of soluble form of mercury (Hg_{tot}) in all stations under investigation, were found to be very low. The highest concentrations were found in Narta Lagoon. Narta Lagoon is a half closed system. Its water communication with sea is very small. On other hand, Narta Lagoon is positioned very near to contaminated site and just in the direction of highest content of mercury in air samples, so as it is expected, the concentration of mercury (mean 0.136; min. 0.112, max. 0.206 ng/ml) in water samples of Narta Lagoon (Stations 1 to 6) were found to be higher than in reference station (Station 7) (0.105 ng/ml). The similar situation were found also in Orikumi Lagoon, where the concentration of mercury (mean 0.094; min. 0.058, max. 0.108 ng/ml) (Stations 14 to 18) differ slightly from reference station in sea (Station 13) (0.085 ng/ml). Based on NIVA Classification, all the stations positioned in lagoons or in Sea (Stations 1 to 18), are not polluted by mercury (the samples of these sites can be classified as 2nd (Orikumi Lagoon and the Sea) or 3rd (Narta Lagoon) Class of Quality.

6.1.2 The concentration of Hg in sediment samples

The concentration of mercury in sediment samples are given in tables bellow.

Table 20 The concentration of Hg in sediment samples of Vlora Bay (mg/kg, DW)

	Station						
Element	*7*	*8*	*9*	*10*	*11*	*12*	*13*
Hg	0.159	0.920	0.107	0.118	0.093	0.137	0.089

Table 21 The concentration of Hg in sediment samples of Narta Lagoon (mg/kg, DW)

	Station						
Element	*1*	*2*	*3*	*4*	*5*	*6*	*7 (Ref. St.)*
Hg	0.086	0.100	0.085	0.064	0.078	0.095	0.159

Table 22 The concentration of Hg in sediment samples of Orikumi Lagoon (mg/kg, DW)

	Station					
Element	*14*	*15*	*16*	*17*	*18*	*13 (Ref. St.)*
Hg	0.081	0.076	0.108	0.086	0.057	0.089

Table 23 Some statistical data about the concentration of Hg in sediment samples of Narta and Orikumi Lagoons (mg/kg, DW)

Lagoon	*Hg*			*Reference samples on Sea*	*The Class of Quality(NIVA Classification) [35]*
	mean	*Min.*	*Max.*		
Narta	0.085	0.064 (4)	0.100 (2)	0.159 (7)	1st Class
Orikumi	0.0816	0.057 (18)	0.108 (16)	0.089 (13)	1st Class

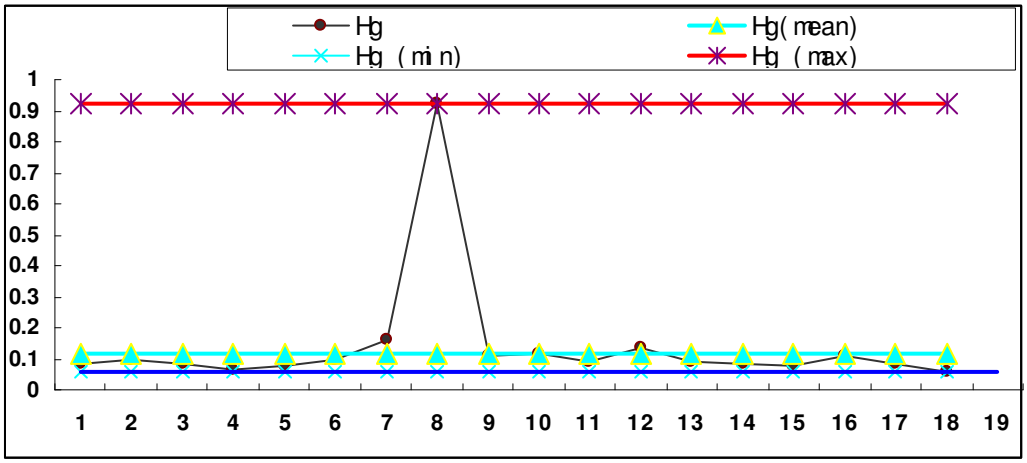


Figure 29 The histogram of Hg distribution in sediment samples (mg/kg, DW)

The concentration of mercury (mean 0.085; min. 0.064, max. 0.1 mg/kg) in sediments samples of Narta Lagoon (Stations 1 to 6) is lower than in reference station (Station 7) (0.159 mg/kg). Station 7 is very close with the contamination site of "Vlora Hot Spot" of pollution, so it appeared to be polluted by mercury. The situation had a small change in Orikumi Lagoon, where the concentration of mercury (mean 0.0816; min. 0.057, max. 0.108 mg/kg) (Stations 14 to 18) are similar with reference station in sea (Station 13) (0.089 mg/kg). Based on NIVA Classification, all other stations positioned on sea (Station 9 to 13), are not polluted by mercury (the sediments of these sites can be classified as 1st Class Quality, or slightly polluted).
As it is expected, the highest concentration of mercury (0.920 mg/kg, DW) was found in station 8, just in "Vlora Hot Spot" of pollution site. Bases on NIVA Classification, all other stations positioned on sea (Station 9 to 13), are not polluted by mercury (the sediments of these sites can be classified as 1st Class Quality, or slightly polluted, except station 8 with very high Hg concentration. Station 8 can be classified as 5th Class Quality, or markedly polluted sediments). Through the data presented in tables above, due to metallic form of mercury pollution and its very small soluble ability, the transport of mercury from contaminated site to Vlora Bay is not appeared to be present yet.

Table 24 Content of Hg in seacoast sediments from 21 stations of Albanian seacoast ***(mg/kg DW)***

DATA	***MARINE AREA***							
	Vlora ALB 5	***Durrës ALB 2***	***Shengjin ALB 1***	***Saranda ALB 6***	***Mat ALB 1***	***Ishëm ALB 1***	***Shkumbin ALB 3***	***Seman ALB 4***
Mean. Conc.	0.314	0.103	0.027	0.110	0.066	0.064	0.048	0.042
Min.	0.052	0.033	0.022	0.041	0.015	0.042	0.034	0.018
Max.	0.920	0.331	0.030	0.158	0.121	0.108	0.079	0.071
N	24	32	8	10	24	18	12	18

Compare with background level of mercury in sediment samples of Mediterranean Sea (0.05-0.100 mg/kg), and the background level of mercury in sediment samples of polluted sites of North Adriatic Sea (0.240-0.600 mg/kg), the background level of mercury in sediment samples of our coastal part (from Shengjini in North to Saranda in Sud) (0.015-0.110 mg/kg, if we do not take in consideration Vlora polluted sites), are the same with Mediterranean Sea (0.05-0.100 mg/kg). Vlora polluted site, with maximum concentration of mercury 0.920 mg/kg, DW, (0.052-0.920 mg/kg) has similar contamination with North Adriatic Sea (0.240-0.600 mg/kg). It is necessary stressing again, that metallic form of mercury contamination has located the contamination site in a very small area just in contact with contaminated soils.

6.1.3. The concentration of Hg in biota samples

There were three types of species under investigation: mussels, macroalgaes and plants species. Fishes and mussels are consumable food of people and very good bio-indicator of mercury and heavy metals contamination, so fish/or mussel samples are very important to be always under control.

Table 25 The mean concentration of mercury in mussel samples collected in different stations of Albanian coast

EL	***COASTAL AREA***						
	Vlorë	***Durrës***	***Mat***	***Sarandë***	***Seman***	***Karavasta***	***Butrint***
Hg ***(mg/kg FW)***	**0.129**	0.040	0.021	0.024	0.061	0.113	0.103

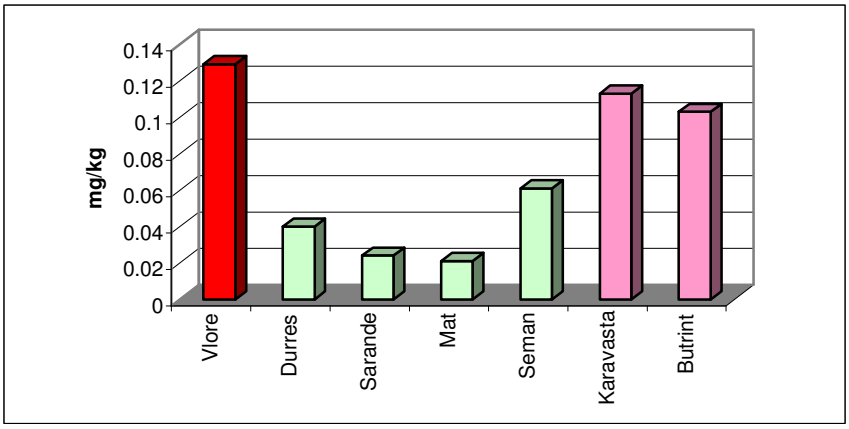


Figure 30. Mercury levels in mussels (Mytilus galloprovincialis) in some Albanian seacoast samples (mg/kg FW)

Compare with concentration level of mercury in mussel samples of South Adriatic Sea (0.035-0.145 mg/kg mg/kg), the concentration level of mercury in mussel samples collected in our coastal part (from Shengjini in North to Saranda in Sud) (0.024-0.129 mg/kg FW, included also the samples from Vlora polluted sites), are the same with the mussels of South Adriatic Sea. The same level of concentration of Hg (0.46-0.48 mg/kg) was found also in fish samples *(Mullus barbatus)* collected in Vlora Bay. This is another reason confirming again that metallic form of mercury contamination in Vlora site has not passed in water and biota samples. Few results for the levels of mercury in marine biota (fish, mussels and algae) show higher levels of

mercury content in samples taken in Vlora Bay comparing to the other marine areas. Nevertheless all our results for fish and mussels are quite lower than maximum allowed level. Due to metallic form of mercury pollution and its very small soluble ability in water, the concentration of mercury in seawater, sediments, biota and plant samples (except the sediment samples of the Station 8) is very low.

7. Conclusions and some Recommendations

Very high concentrations of mercury in the territory of former plant present a real thread to the residents living very near this territory. The Hg contamination in soils is bound to the unsaturated zone of the area concern: the thickness of the unsaturated zone ranges between about 1.2 and 2.0 m. Hg content in soils decreases with the depth, and at a depth of about 1.5 m below ground level, Hg occurs in the units of $mg.kg^{-1}$.

The most contaminated area remains PVC and Electrolysis plant. Due to transport of soils from seaside to PVC and Electrolysis Plant, the content of Hg in seaside is smaller. After this process, the content of Hg in different deepness appeared to be very critic; till 1.5 m deep Hg content is very high (PVC and Electr.Plant)

The content of Hg in most contaminated area is very high (goes some hundred mg/kg). It consists mainly in metallic Hg form, so the analysis of the speciation of different forms of Hg in soils is difficulty to do. The distribution of metallic mercury in soils is not homogeny, so the samples are not homogeny, too. For these reasons, the reproducibility of the analysis is very poor.

The estimated volume of the soils with concentration of Hg higher than 20 $mg.kg^{-1}$ amounts to 32,750 m^3 in the area concern.

Compare with previous monitory studies, the content of total Hg in seawater samples appeared to be in the same level (110-140 ng*ml-1). It means that Hg pollution in Vlora Bay, remain to be problem for a long time in the future (Vlora Bay is a half closed Bay). The content of MeHg in seawater samples is about 15% higher than before, so methylation process is present

Our monitoring studies proved that there was not evidence any distinct contamination from mercury in Vlora Bay caused by former Soda-PVC plant. The concentrations of mercury compare with levels in the polluted areas of Northern Adriatic, in e sediments, seawater and biota (fish, mussels and algae) samples were found to be lower, except the site near the former plant. The hydrological factors that actually control the distribution of Hg in the sediments of the Bay are not favorable for the transportation of Hg to the open sea, because Vlora Bay is a semi closed area having just little communication with open sea. These factors necessities a long term monitoring program for mercury levels in sediments, water and biota samples.

The overall mean of mercury content in hair samples of exposure people (0.806 μg/g) was bellow the range of 1-2 μg/g decided by WHO as normal range for the population which does not consume fish with high methyl mercury content. The highest value found (1.953 μg/g) is within this interval, too, but compare with overall mean of mercury content in hair samples of un-exposure people (0.402 μg/g) the so mentioned values of exposure people are two times higher. The most critical group is the second group, the children 2-12 years old, (N=37), where 75% of them belong to the range up to 0.5 μg/g (33% of them belongs to the range 1-2 μg/g and about 42% of them belong to the range 0.5-1 μg/g). The mean content of Hg in hairs of exposure people was found to be 2 to 3 times higher than the same age and sex of the un-exposure people. Aiming to have more precise conclusions about the affect of metallic mercury

to the people living inside and surround contaminated territory, the analysis of the urine samples (as better bio-indicator for metallic mercury affect to the people) should be done to the children.

References:

[1] G. Gjyli (2003), "Metodologie di monitoraggio marino della Baia di Valona", in "Revitalisation of the land contaminated with mercury in the area of production of Cl PVC in Vlora, Albania", Tirana, 7/8 February 2003

[2] A. Çullaj, V. Çelo, D. Babi (2000), "Analytical Investigation of Heavy Metals Content in Sediments of Albanian Coast", Journal of Environmental and Ecology, 1, No 1, 81-89,

[3] D. Babi (1996), "Determination of Total and Organic Mercury, and Some Other Heavy Metals in Biota and Marine Sediments", Ph. D. Thesis, Faculty of Natural Sciences, University of Tirana

[4] Babi D., Çullaj A, Çelo V., Pano N. (1998), "Evaluation of the Heavy Metals Pollution of the Sediments of Vlora Bay, Adriatic Sea, Albania", Fresenius Environ., Bull., No 7, 577-584

[5] V. Çelo, D. Babi, B. Baraj, A. Çullaj (1999) "An Assessment of Heavy Metal Pollution in the Sediments Along the Albanian Coast", Water, Air and Soil Pollution, 111, 235-250

[6] Baraj B., Çocoli V., Çullaj A., Babi D., Robinson D. (1994) "The Heavy Metals Content in Sediments, Biota and Macroalgae Samples Collected at Vlora Bay", Fresenius Environ. Bull. 3: 169-174

[7] P. Lazo, A. Çullaj (2002), "Determination of the Different States of Mercury in Seawater near the Vlora and Durres Bays", Anal. Bioanal. Chem., 374: 1034-1038

[8] UNEP, MAP Long-Term Programme for Pollution Monitoring and Research in the Mediterranean Sea. MED POL II National Monitoring Programme, Albania, (1992-1998)

[9] Results of the MED POL II Programme for Albania -Internal Reports of the Section of Analytical Chemistry, Faculty of Natural Sciences, University of Tirana, (1992-1998)7) UNEP MAP Technical Reports Series No 86, Athens, (1994)

[10] Jeftic L., M. Bernhard, A. Demetropoulous, F. Fernex, G. P. Gabrielides, F. Gasparovic, Y. Halim, D. Orhon and L.J.Saliba: (1990), "State of the Marine Environment in the Mediterranean Region", UNEP Regional Seas Reports and Studies, MAP Technical Reports Series No 132, Athens

[11] UNEP: State of the Mediterranean Marine Environment. MAP Technical Reports Series No 28, UNEP, Athens, 1989

[12] UNEP Chemicals: "Global Mercury Assessment" IOMC, Geneva, Switzerland, December 2002

[13] Çullaj A, Bozo Dh., Baraj B. (2003), "An assessment of mercury situation in Vlora Bay", GEF/SGP Project, Tirana

[14] P.Lazo, A.Cullaj, B.Baraj, An evaluation of Hg, Cr and Heavy Metals pollution in seawater and sediments of Durres Bay Adriatic Sea – Albania, J.Phys. IV France, 107, 715-720 (2003)

[15] P.Lazo, F.Lubonja, A.Arapi, L.Pjeshkazini, An evaluation of heavy metals content in Orikumi, Dukati Bay-Ionian Sea – Albania, International Journal of Chemistry, (IJCS) Vol.2(1), 101-107 (2004)

[16] P.Lazo, The determination of trace levels of mercury in sea water samples, Journal of Environmental Protection and Ecology, No 2, 625 (2001)

[17] UNEP/IAEA Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry. Reference Methods for Marine Pollution Studies No. 26, UNEP 1985

[18] UNEP Balkans Analytical Results – Albania 4/15 (1994)

[19] J.Reif, J.Prusa, V.Mejstrick, et.al., Materials and Geoenvironment (Mercury as Global Pollutant, Part 1), No.1, 220-228 (2004)

[20] B.Ostrosi, A.Grazhdani, et.al, Industrial Levels of Albanian Minerals, Monography, University of Tirana, Faculty of Geology and Miner Sciences, pp. 396-461, 582 (1999)

[21] *P. Lazo, A.Cullaj, A.Arapi, L.Pjeshkazini, P.KotoriActual situation of mercury contamination in "Vlora Hot Spot" area, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[22] *Revitalization of Land Contaminated with Mercury in the Area of the Former Production of Cl-PVC in Vlora, Albania, J. Reif et al.GEOtest Brno, Czech Republic, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[23] *A.Cullaj, P. Lazo,B.Baraj, L.Pjeshkazini, The impact of "Vlora Hot Spot" area to Narta Lagoon, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[24] *P.Lazo, L.Pjeshkazini, F.Malaj Hg content in hair samples of the people living inside "Vlora Hot Spot" area., Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[25] *S.Lacej, A.Cullaj, The determination of metallothionines in mussel samples of Vora and Durres Bay S.Lacej, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[26] *Hydrogeology of the Affected Area. GeoTest, Brno, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[27] *Geophysical Survey of the Polluted Area. GeoTest, Brno, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[28] *Study of Remote Sensing Images of the Wider Area of Vlora. GeoTest, Brno, Workshop on Vlora "Hot Spot Pollution", 26-27 Appril,2005, Tirana, Albania*
[29] *WHO., Methil Mercury, 1990*
[30] *S.J.haswell, Atomic Absorption Spectroscopy, Theory, design and Application, Elsevier Publisher, (1991)*
[31] *Y.Takizara, M.Osame, Methylmercury poisoning in Minamata and Niigata, Japan Public Health Association, October, 2001*
[32] *O.Malm, The science of total environment, 1995*
[33] *L.Knobeloch, Environmental Health Perspectives, Vol. 103, No. 6, 1995*
[34] *T.W.Clarkson, Environmental Health Perspectives, Vol. 100, 1992*
[35]

SPECIFIC SUPPORT ACTION

BIOMERCURY

Worldwide remediation of mercury hazards through biotechnology

NMP2-CT-2004-505561

Priority 3 NMP: Nanotechnology and nanosciences, knowledge based multifunctional materials, new production processes and devices

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Deliverable D15

Case Study 4
Coal Fired Power Plants & Municipal Waste Incinerators

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RE	Restricted to a group specified by the consortium (including the Commission Services)	✓
CO	Confidential, only for members of the consortium (including the Commission Services)	

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Executive Summary

This report summarises the results of a case study on coal-fired power plants and municipal waste incinerators that was conducted with a view to assessing the applicability of the *BIOMER* microbial bioremediation process for the treatment of waste waters arising from these industries. Wet Flue Gas Desulphurisation (FGD) systems, also known as 'wet scrubbers', are commonly installed at coal-fired power plants and waste incinerators to remove acid gases (sulphur dioxide, hydrogen chloride) from the flue gas stream. In addition, wet scrubbers are also able to remove a significant proportion of mercury from the flue gas. Dissolved mercury in the scrubber effluents may be treatable by the *BIOMER* process, but little information is available in the public domain on how high the mercury concentrations in these effluents are. In order to be feasible as an alternative treatment option, *BIOMER* requires dissolved aqueous mercury concentrations to be in the milligram per litre range. Data was therefore collected from industry via personal contacts and direct sampling, to assess the scope for a potential application of the process. This report gives an overview of the fate of mercury in coal-fired power plants and municipal waste incinerators, the magnitude of Hg emissions to air and water, typical wet scrubber configurations, and commonly employed treatment processes for the waste waters arising from the FGD unit. Data on mercury concentrations in scrubber liquids is summarised and the feasibility of the *BIOMER* process is assessed. Large volumes of wastewater are generated at power stations, and mercury concentrations in the effluents are generally lower than 0.5 mg/l and more typically in the order of 0.002 – 0.02 mg/l. A lot of the mercury in power station flue gases is in the elemental form and is not captured by the scrubber. At municipal waste incinerators, on the other hand, most of the mercury in the flue gas is present in oxidized (water-soluble) form and is efficiently captured by the scrubber. Mercury concentrations in the effluents from waste incinerators are therefore much higher and are in the milligram per litre range. Treatability studies were successfully carried out for these effluents at a variety of concentrations. However, since other contaminants such as cadmium and lead are also present, the *BIOMER* process by itself would not be sufficient and would have to be incorporated into a wider treatment train that is capable of dealing with all pollutants occurring in these waste waters.

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Case Study 4:
Coal Fired Power Plants & Municipal Waste Incinerators

1. Background

Mercury is a persistent, globally cycling pollutant that readily accumulates in the food chain. Because of its toxic and bioaccumulative nature and its capacity to affect even remote areas that are far from industrial point sources, mercury has been identified as a priority air pollutant and is listed as a priority hazardous substance in the Water Framework Directive [1, 2].

Fossil fuel combustion is the largest source of atmospheric mercury world-wide and accounts for three quarters of anthropogenic mercury emissions in Europe and about 30-40% of emissions in the United States [3, 4]. Municipal and medical waste incinerators are also significant sources, although their relative importance has declined in recent years due to the implementation of stricter emission controls. Together, coal-fired power plants and waste incinerators account for approximately 1500 tonnes, or 70%, of annual anthropogenic mercury emissions [5]. About 15% of global anthropogenic emissions of mercury are thought to be attributable to Europe [6].

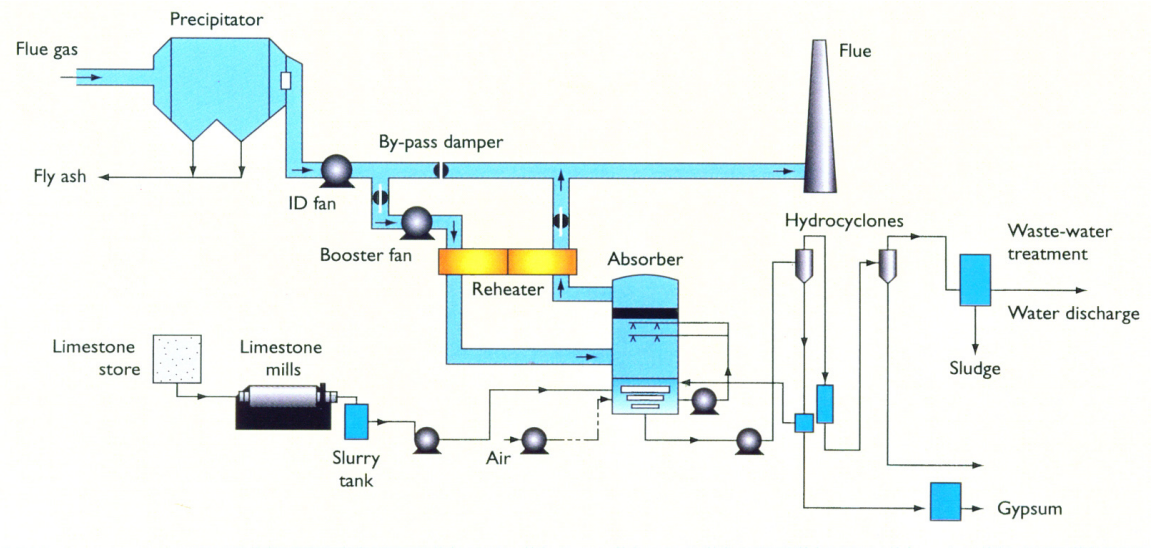
The EU Mercury Strategy [7] envisages a number of actions to protect human health and the environment, and stresses the need for reducing European emissions of mercury. The increasing implementation of control technologies – driven by recent changes in legislation – is expected to lead to a significant drop in emissions of hazardous air pollutants both from large power plants and municipal waste incinerators over the coming years. Wet Flue Gas Desulphurisation (FGD) systems that are primarily installed at plants to remove sulphur dioxide (SO_2) and other acid gases from the flue gas stream offer the added advantage that they are also able to remove a large proportion of the mercury. Dissolved mercury in the waste water effluents arising from the operation of wet scrubbers is potentially treatable by the new *BIOMER* bioremediation process. This case study investigated the scope for a potential application of this environmentally friendly and cost-effective technology in the power industry and waste incineration sector.

2. Assessment of pollution problem

2.1 Localization

2.1.1 Coal-fired power stations

Flue Gas Desulphurization (FGD) systems are widely employed at power stations to remove gaseous sulphur dioxide (SO_2) from coal combustion flue gases. Wet FGD systems (also known as wet "scrubbers") include the conventional lime/limestone scrubbers and less common systems such as dual alkali, seawater, sodium carbonate, magnesium-enhanced lime or ammonia scrubbers. Lime/limestone scrubbers have become the leading wet FGD system worldwide and are extensively used at large utility boilers. The use of wet scrubbers is expected to increase further in response to recent regulatory changes in the U.S. (CAIR & CAMR) and in Europe (Large Combustion Plants Directive, LCPD) [8, 9]. Apart from SO_2, wet scrubbers can remove significant amounts of mercury from flue gases as a 'co-benefit'.

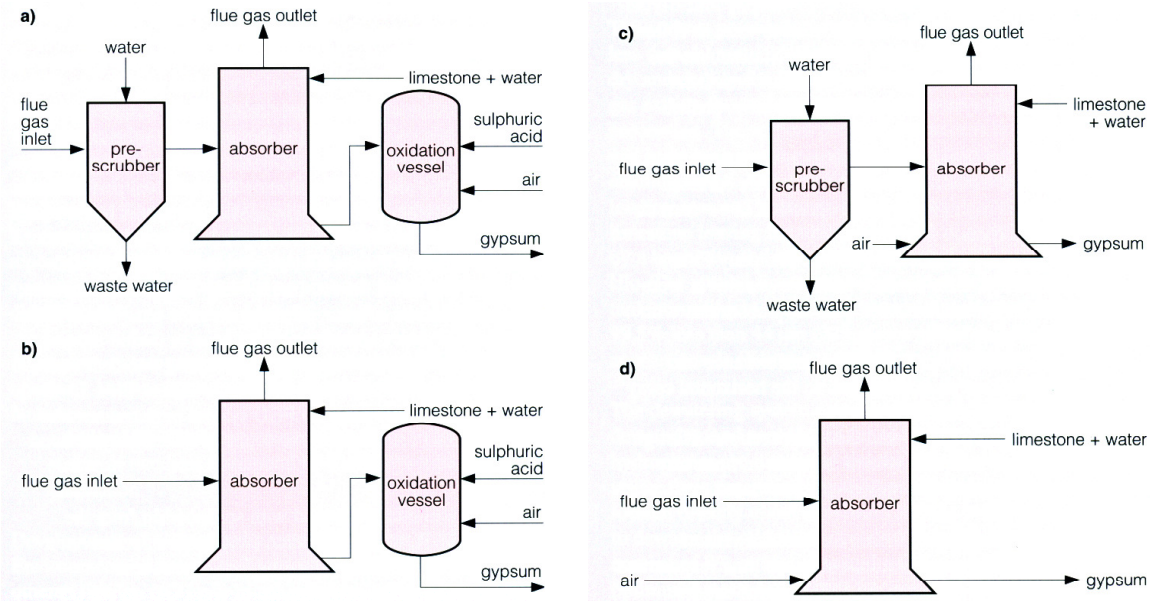


(Source: DTI, 2003)

Fig. 1: General Scheme of the Limestone-Gypsum FGD Process

Fig. 1 gives a general overview of the limestone-gypsum process [10]. Having passed an electrostatic precipitator that removes fly ash and dust particles, the flue gases from the combustion process enter the FGD (typically a spray tower absorber) where they are scrubbed with an alkaline limestone (calcium carbonate) slurry to remove the SO_2. In addition the process removes all HCl from the flue gas. The formed sulphite salts are oxidized further to sulphate and precipitate out of solution, yielding a saleable by-product (gypsum). The cleaned

flue gas exits the absorber through de-misters and is reheated prior to discharge through the stack. The gypsum slurry is extracted from the absorber sump, thickened, de-watered (typically by hydrocyclones or vacuum belts) and washed for subsequent storage. During normal process operation there is a build-up of impurities in the process liquor, which is due to fly ash carryover from upstream, calcium chloride from HCl in the flue gas and other impurities that are concentrated on recycle. The system is purged with water to reduce these contaminants [10].

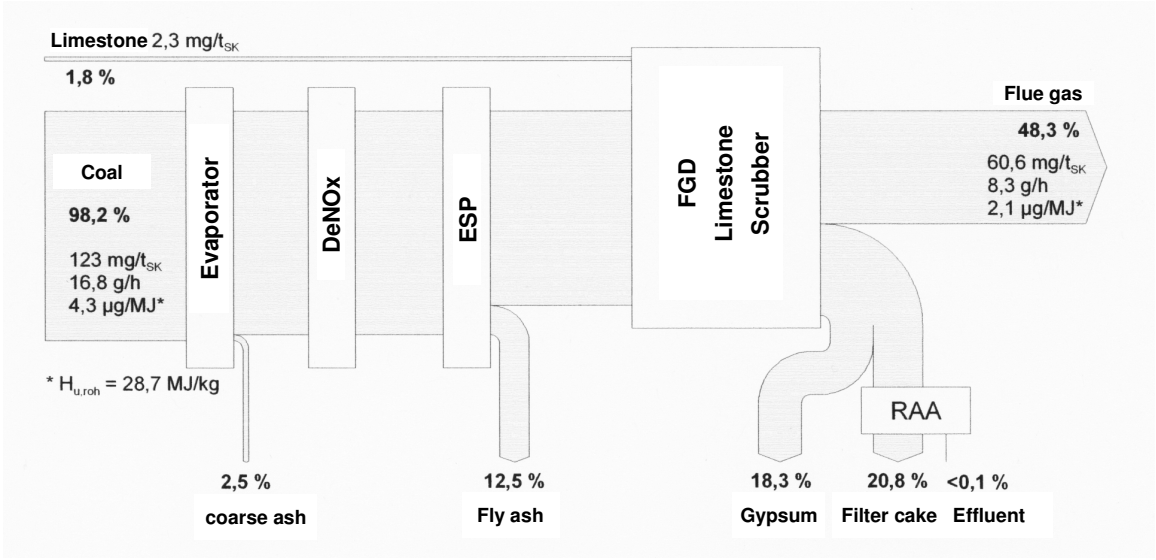


(Source: IEA Coal Research, 1998)

Fig. 2: Wet scrubber configurations at coal-fired power stations

Some plants employ a pre-scrubber to remove acid gases (HCl and HF). Fig. 2 illustrates some common configurations for absorber-only and pre-scrubber combinations [11]. A low pH pre-scrubber has the advantage of removing more mercury as well as any fine particulates which may be carrying other trace elements, thereby yielding a higher quality gypsum product. Many of the older systems in Europe were originally designed as pre-scrubber systems, but are now gradually being phased out. Simpler configurations of wet limestone scrubbers where all chemical reactions occur in an integrated single absorber are most popular for retrofit applications, e.g. in Germany and in the U.S., and are now the leading FGD system [12].

An example of the mass flow of mercury through a typical coal-fired power plant equipped with a two-phase wet limestone scrubber is shown in Fig. 3. The results of this study show that despite the presence of the FGD, a large part of the mercury is still emitted from the stack [13].



(Source: Hein et al., 2002)

Fig. 3: Estimated mass flow of mercury in a coal-fired power plant with a wet FGD

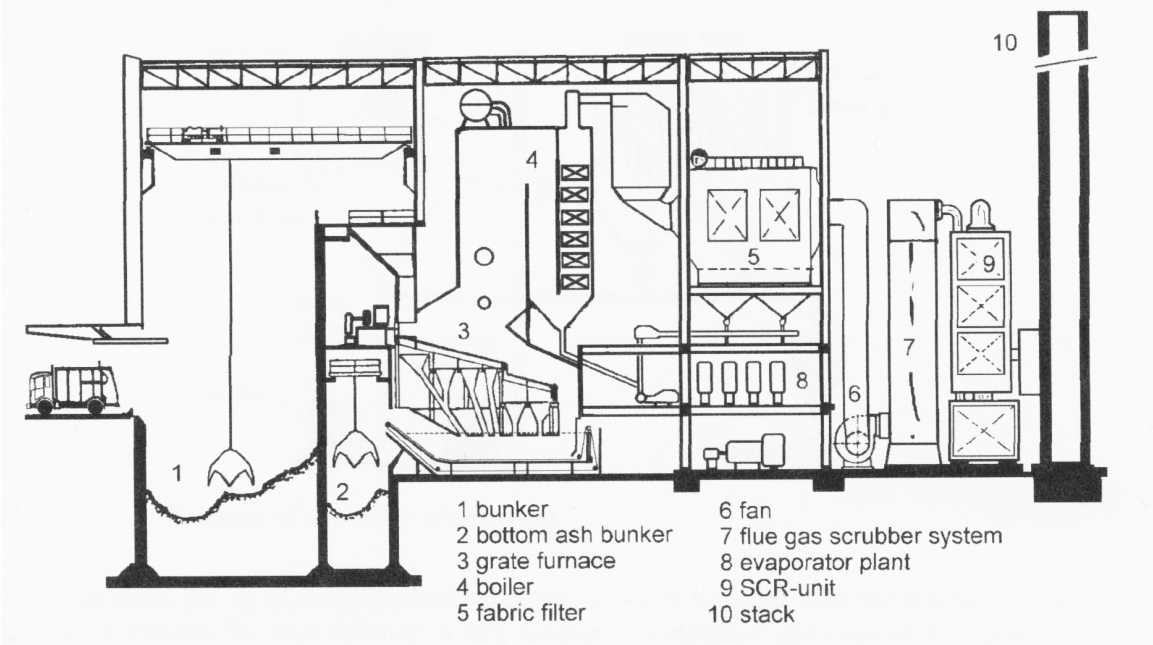
Mercury concentrations in the flue gas before the scrubber were 5 – 7 µg/m^3 and the overall removal efficiency of the wet limestone scrubber was 45%. The residual mercury concentration in the gypsum product was 0.74 mg/kg. Only a small fraction of the overall mass of mercury flowing through the plant was found in the effluent (<0.1%). In a similar study conducted at a plant with essentially the same configuration during co-incineration of sewage sludge, the share of mercury in the effluent was ~3% [13]. Lime/limestone-gypsum based FGD systems in the Netherlands removed between 30-78% (average 54%) of mercury from the flue gases [14]. Mercury removal efficiencies at power stations are highly plant-specific, which gives rise to large variations in reported emission reductions.

2.1.2 Municipal waste incinerators

In contrast to coal-fired power stations, mercury removal efficiencies of 80 – 90% are routinely achieved by wet scrubbers at waste incinerators. This is mainly due to the combined effect of higher mercury concentrations in the flue gases and relatively high chloride concentrations which transform the mercury into a more soluble form (cf. section 2.2.2).

Fig. 4 illustrates the general process scheme for a municipal solid waste incinerator equipped with a flue gas cleaning system [16]. The particulate control device upstream of the scrubber system is in this case a fabric filter, but it could also be an electrostatic precipitator. Downstream of the scrubber there is typically a stage for the removal of nitrogen oxides (SCR-unit). The cleaned flue gases are released into the atmosphere via the stack.

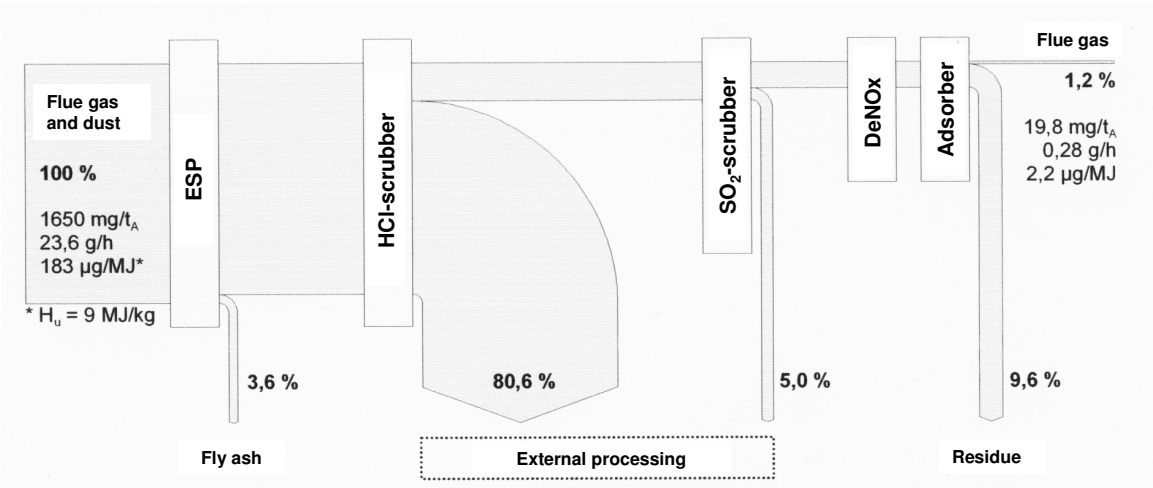
The flue gas system shown in Fig. 4 is only one of several systems available. In most large-scale plants, wet separation of HCl, HF, and SO_2 is employed, but dry FGDs are also common at incinerators. The latter yield a solid residue for disposal instead of waste water.



(Source: Achternbosch and Richers, 2002)

Fig. 4: Scheme of a municipal solid waste incinerator with flue gas cleaning system

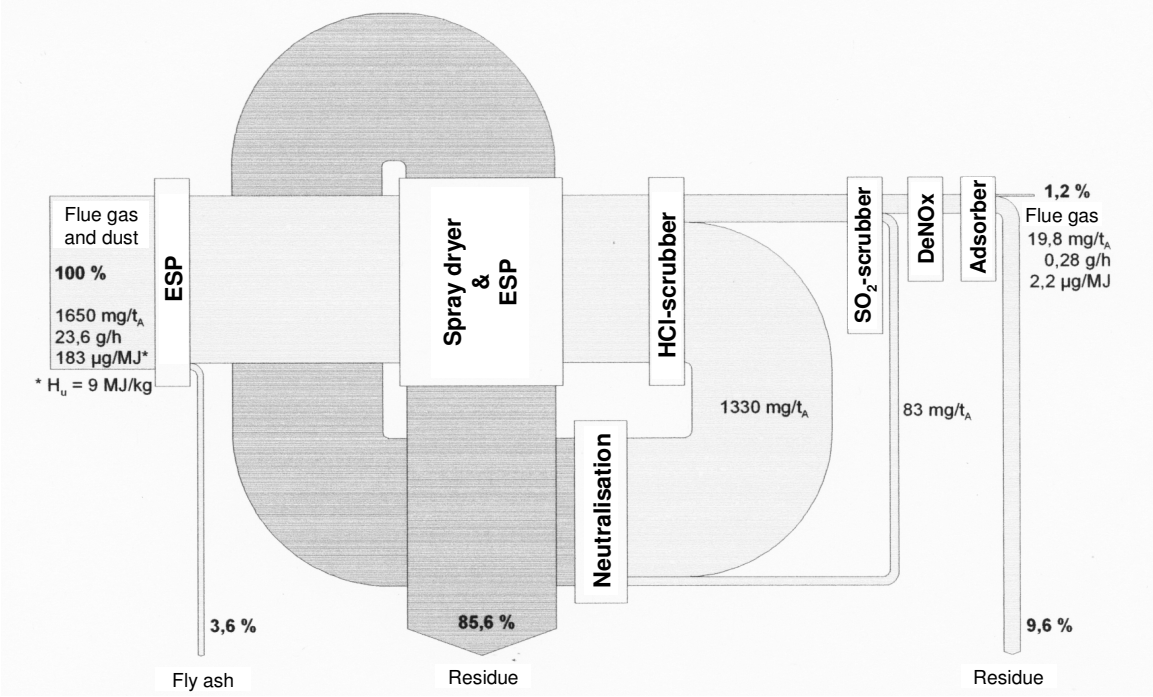
A typical two-stage wet FGD system at incinerator plants consists of a HCl-scrubber and a SO_2-scrubber, as shown in Fig. 5. In the first scrubber stage, the acid gases HCl and HF are separated from the flue gas. Mercury is also strongly absorbed into the aqueous phase which has a pH <1. No auxiliary chemicals are needed. The second scrubber stage operates at neutral pH and serves to separate SO_2 from the flue gas. Auxiliary chemicals (sodium hydroxide, calcium hydroxide / carbonate, and dolomite) are added to maintain a pH of 7. The separation efficiencies of the two stages with respect to mercury in a typical German incinerator (MSWI Bamberg) are given as 83.5% for the HCl-scrubber and 32.9% for the SO_2-scrubber [16].



(Source: Hein et al., 2002)

Fig. 5: Estimated mass flow of mercury in a model MWI plant of configuration 1

The fate of mercury in a municipal waste incinerator is illustrated in Fig. 5 and 6 for the two most common wet scrubber configurations [13]. An example of configuration 1 is the MSWI Bamberg. Configuration 2 differs by the insertion of a spray dryer between the electrostatic precipitator (ESP) and the HCl-scrubber. In both cases, the majority of the mercury is separated from the gas stream in the HCl-scrubber. The principal difference is that in configuration 2, the mercury-enriched wastewater is evaporated in the spray dryer after treatment (cf. section 3.1.1), yielding only solid residues for disposal.



(Source: Hein et al., 2002)

Fig. 6: Estimated mass flow of mercury in a model MWI plant of configuration 2

2.2 Dimension

Industrial emissions to air and water are increasingly being monitored in Europe and the information is made publicly available on national registers and on the European Pollutant Emission Register, EPER [17]. In 2004, combustion facilities with a thermal output greater than 50 MW from 25 European countries reported aerial emissions of mercury in excess of 12 tonnes and emissions to water of ~0.6 tonnes, representing 38% of Hg emissions to air and 12% of direct emissions to water from all industrial sectors. Facilities for the disposal and recovery of hazardous or municipal waste – which are mainly incinerators – reported 1.77 tonnes of aerial Hg emissions, and 0.07 tonnes to water. It is important to remember that releases from smaller installations that fall below the EPER reporting thresholds of 0.01 tonnes per year to air and

0.001 tonnes per year to water are not included in these estimates. From the above figures it is evident that more than 95% of mercury emissions from the power industry and waste incineration sector are to air, and less than 5% to water.

2.2.1 Coal-fired power stations

Mercury concentrations in coal vary widely depending on the coal type and country of origin, but are generally below 0.1 mg/kg. On combustion, practically all of the mercury that is present in the coal is released in vapour form into the flue gas. Mercury concentrations in flue gases in various types of coal-fired boilers and different countries are typically in the range 4 – 10 µg/m^3. In the flue gas, mercury can be present in various chemical forms (species). Gaseous elemental mercury (Hg^0) typically comprises about 50-60% in power plants. Oxidised mercury (mainly consisting of Hg^{2+}) can range from 20-80% and is most frequently ~40%. The fraction of mercury bound to particles (Hg_p) is generally less than 5%.

Mercury removal efficiencies by wet scrubbers vary widely and are primarily dependent on the form of Hg in the flue gas: Oxidized Hg species are highly water-soluble and can be efficiently (>90%) captured in the scrubbing solution, but elemental mercury vapour is insoluble and is not retained. A large number of factors such as coal type, co-installed air pollution control equipment such as DeNOx and operating conditions directly or indirectly affect the performance of scrubbers through their impact on Hg speciation in the flue gas [15].

No limit values have been set to date for aerial emissions of mercury from power plants, despite the fact that they are the largest source of atmospheric mercury emissions in the EU. However, in view of the fact that the U.S. recently regulated mercury emissions from the utility industry [8], it is not unlikely that the EU may eventually follow suit. In the meantime, some reductions in mercury emissions are expected to be achieved as 'co-benefits' through the installation of equipment to control emissions of sulphur dioxide, nitrogen oxides and particulate matter that will be necessary for combustion plants >50 MW to comply with the permitting rules of the IPPC Directive and the Large Combustion Plants Directive [18, 9].

Wet scrubbers at power stations generate large volumes of wastewater, typically about 50 m^3/h per absorber. Mercury concentrations in these effluents generally range between 0.05 and 0.8 mg/l and are discussed in more detail in section 3 (cf. Table 1 and Table 3).

2.2.2 Municipal waste incinerators

Mercury concentrations in flue gases from municipal waste incinerators are several orders of magnitude higher than in power stations (200 – 500 µg/m^3), which is due to the higher mercury concentrations in waste compared to coal and the lower volumes of gas that are generated. A

comparison with the current emission limit value of 0.05* mg/Nm^3 prescribed by Directive 2000/76/EC [19] for flue gases from waste incineration shows that incinerator flue gases definitely require treatment to be compliant with the limit.

Incinerator flue gases contain a much larger proportion of mercury (usually between 70-80%) in the oxidised form (Hg^{2+}), whereas gaseous elemental mercury (Hg^0) comprises only about 20%. This together with the low operating pH of the HCl-scrubber greatly increases the capture efficiency of mercury by scrubbers at waste incinerators.

The new EU Directive on waste incineration sets an emission limit value for mercury and its compounds of 0.03 mg/l (in unfiltered samples) for discharges of waste water from the cleaning of flue gases [19]. Pollutant concentrations in wastewater have to be determined both *before* and *after* treatment, and the dilution of wastewater for the purpose of complying with the emission limit values is not allowed.

Amounts of effluents arising from scrubbers at municipal waste incinerators are in the order of 300 l/t_{waste} [16]. Mercury concentrations in these effluents are generally in the milligram per litre range and are discussed in more detail in section 3 (cf. Table 2 and Table 4).

2.3 Gaps of knowledge

Most of the information submitted to the European Pollutant Emission Register, EPER [17] depends on rather crude estimates or mass balance data, since few power stations are currently capable of monitoring mercury emissions. There is also a general shortage of data on mass balances around flue gas cleaning systems as these measurements are not part of the routine monitoring undertaken at power stations or waste incinerators. Existing balances have therefore sometimes been supplemented with model calculations. Furthermore, substance flows and mercury removal efficiencies are highly site specific and are to a large degree influenced by specific plant configurations and operating conditions, therefore it is difficult to draw general conclusions.

A major problem that still needs to be resolved before the mercury capture efficiency of wet scrubbers can be improved is that the absorbed Hg^{2+} is not stable in the scrubber liquor. It has been found that some of the dissolved Hg^{2+} captured in scrubbers can be reduced to volatile Hg^0 by aqueous sulfite and/or bisulfite species and is then re-emitted to the gas phase [20]. The factors influencing Hg species transformations in scrubbers are not well understood. SOTON is planning to conduct further studies on this.

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*In Germany a stricter limit of 0.03 mg/m^3 applies for the incineration of wastes.

3. Solutions - treatment options including costs

3.1 Description of currently used treatment methods

An extensive overview of the current state of knowledge on control technologies for mercury emissions from coal-fired power plants and municipal waste incinerators has already been given in the D14 report - Assessment of Control Options for Mercury [15]. This section therefore focuses only on currently used methods for the treatment of waste waters arising from wet scrubbers, which is of direct relevance for the assessment of the applicability of the *BIOMER* technology.

3.1.1 Coal-fired power stations

The most commonly employed wastewater treatment system at power stations involves three main stages: Precipitation and pH adjustment, flocculation and coagulation, sludge thickening and dewatering. Usually this is carried out in a series of linked tanks where all treatment chemicals are added to a continuous flow of water. An outline of a generic system for a FGD plant is shown in Fig. 7.

Stage 1 – Precipitation and pH Adjustment

This involves the addition of sodium hydroxide or lime slurry (cheaper) to raise the pH to 8.5 – 9.0 and precipitate the metals as their insoluble hydroxides. As the solubility of metal hydroxides varies with the metal and the pH of the solution, it is not possible to reduce all metals to their discharge limit concentrations by this procedure. A second stage precipitation is carried out by sulphide, either sodium sulphide or an organo-sulphide such as tri-mercapto-triazine (TMT 15) which is less toxic than sodium sulphide. Sulphides of metals, including mercury, are extremely insoluble, therefore very low residual concentrations are achieved. (Some plants are able to meet their discharge limits without this secondary precipitation stage.)

Stage 2 – Flocculation and Coagulation

A coagulant (typically ferric chloride) is then added to form a micro floc which captures the fine particulates and precipitates. The poly-electrolyte is added to assist the formation of larger floc particles which will settle under gravity. The suspension of floc particles is passed into a settler, where the floc settles as a sludge and clean water is taken off for subsequent filtration. Sludge settlement may be by a circular scraper settler, or a lamella plate separator. Alternatively, dissolved air flotation can be employed where the sludge is skimmed off at the top.

The subsequent multi media filtration removes the last traces of particulate matter and the water is transferred to a final storage tank or basin. A final pH adjustment stage, acid dosing, is included to meet the typical pH 6 – 9 discharge limit. This may be achieved by recirculation around the storage tank. This tank also provides filter backwash water. The waste from filter backwash is recycled to the front of the waste water treatment plant.

Stage 3 – Sludge Thickening and Dewatering

The sludge is extracted from the settler by intermittent pumping to a sludge thickener. Sludge entering the thickener has only 2 – 4% solids content. In the thickener it is concentrated by further settlement, and addition of chemicals, to achieve around 10 – 20% solids content. The thickened sludge can be either directly fired to a boiler as a slurry or it can be transferred to a sludge dewatering system.

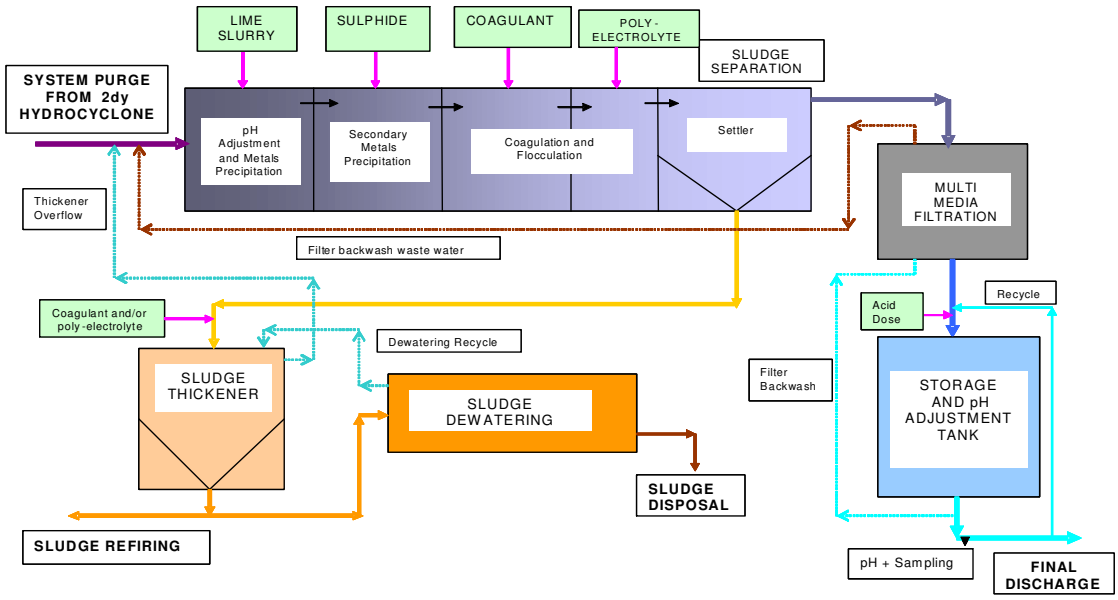


Fig. 7: Process Flow Diagram of Generic FGD Waste Water Treatment Plant

Typical ranges of several important constituents of FGD waste waters are given in Table 1. It is evident that metal concentrations before treatment are highly variable and depend on many factors, including the type of power plant, air pollution control equipment, absorber type, coal type, etc. The given values only serve as a broad guide and concentrations outside the stated ranges are also frequently found.

Table 1: Typical ranges of some metals in FGD waste water before and after treatment, and typical discharge limits in the U.K.

Parameter	Before, mg/l	After, mg/l	Typical maximum discharge limit, mg/l
Aluminium	50 – 800	<2.0	3 – 3.5
Arsenic	0.05 – 3.0	<0.05	0.05 – 0.1
Cadmium	0.04 – 0.5	<0.1	0.025 – 0.5
Chromium	0.3 – 5.0	<0.1	0.5 – 1.0
Copper	0.1 – 0.85	<0.1	0.15 – 0.2
Iron	30 – 400	<0.5	1.5 – 2.0
Mercury	0.05 – 0.8	<0.05	0.02 – 0.03
Nickel	0.2 – 6.0	<0.1	0.2 – 0.4
Lead	0.1 – 3.0	<0.1	0.2 – 0.5
Selenium	0.2 – 1.0	<0.2	0.15 – 0.5
Zinc	0.4 – 8.0	<0.1	0.5 – 1.0

Source: IEA Coal Research [11] and pers. commun.

Discharge limits in the U.K. are set on a site-specific basis according to plant performance and the receiving waters. Typical maximum discharge limits for mercury are in the range 20 – 30 µg/l. One plant has a limit of 50 µg/l, but routinely achieves <2 µg/l in their effluents even without the use of TMT.

3.1.2 Municipal waste incinerators

Waste waters arising from wet scrubbers in waste incineration plants are treated in a very similar way to those in power stations (see above), but the total volume of waste water is a lot lower and the chemical constituents are much more concentrated. This is the reason why higher mercury concentrations are found in these effluents. Note that waste water is only generated in plants of configuration 1 (Fig. 5 in section 2.1.2). In configuration 2, the treated effluent is evaporated in the spray dryer, yielding only dry residues which are separated off in a secondary ESP.

In a typical treatment plant, most of the heavy metals in the effluent from the HCl-scrubber are precipitated as hydroxides in the neutralization step where an excess of $Ca(OH)_2$ is added. About 20% of the sulphur is co-precipitated here as gypsum. Since mercury is insufficiently separated, it has to be precipitated in a subsequent step using sulphur-containing chemicals (typically TMT 15, Nalmet A1, or Na_2S_x). The precipitation agents can be added either in the

wastewater treatment plant, or they can be dosed directly into the flue gas before the acidic scrubber.

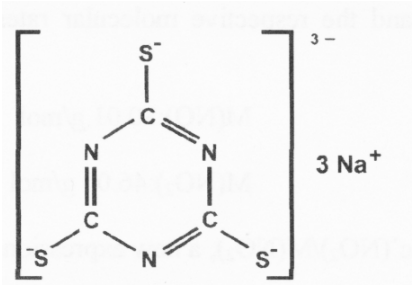


Fig. 8: Chemical structure of tri-mercapto-triazine (TMT 15)

After settling, the $CaCl_2$-containing filtrate is pumped to the 're-salting stage' where it reacts with the $NaSO_4$-rich scrubber liquid from the SO_2-scrubber and relatively insoluble $CaSO_4$ is formed. After the subsequent crystallization step, a second treatment with TMT removes any residual heavy metals. The gypsum is pumped to the sludge settler and the sludge is dewatered e.g. in a centrifuge.

The following table gives an example of typical concentrations for the three most important heavy metals that occur in untreated effluents from wet scrubbers at incinerators.

Table 2: Typical concentrations of selected chemical constituents in scrubber liquids at a German waste incineration plant (MSWI Bamberg)

Parameter	HCl-scrubber, mg/l	SO_2-scrubber, mg/l
Chloride	14400 – 32000	4100 – 15100
Sulphur	133.3 – 1300	17980 – 23440
Mercury	6.89 (average)	1.8 (average)
Cadmium	0.59 (average)	0.89 (average)
Lead	13.5 (average)	3.73 (average)

Source: [21]

3.2 Applicability of microbial clean-up technology

3.2.1 Coal-fired power stations

Mercury concentrations in FGD waste waters from coal-fired power stations are highly variable (Table 3). Both the results of our survey of the technical literature and the analysis results obtained for samples collected from power stations in the U.K. and in Germany indicate that mercury concentrations in waste water effluents arising at power plants are not sufficiently high to make the *BIOMER* technology a feasible treatment option. Also, mercury in the absorber slurry appears to be mostly bound to solids (gypsum and fly ash particles). In pre-scrubbers, Hg is mostly in dissolved form and concentrations are higher, but are still generally <0.5 mg/l.

Table 3: Comparison of mercury concentrations found in FGD wastewater at coal-fired power plants before treatment

Country	Hg, mg/l	Source
Europe	0.05 – 0.8	[11] after Mierzejewski 1991
Germany	<1	[11] after Beiers and Weinig 1995
U.K.	<2	[11] after Evans and Grist 1993
Netherlands	0.332 – 0.475 (THg) 0.00065 – 0.004 (diss. Hg) 0.331 – 0.471 (Hg_s)	R. Meij, pers. commun.
Germany	Absorber: <0.00005 – 0.0047 (diss. Hg) 0.017 – 0.031 (Hg_s) Pre-scrubber: 0.280 – 0.336 (diss. Hg) 0.005 – 0.011 (Hg_s)	Gutberlet 1984 [22]
U.K.	Absorber: 0.5 Pre-scrubber: 1.5	[11] after Hebbs and Cooper 1991
Netherlands	Absorber: <0.070 (day 1) 0.020 – 0.030 (day 2) Pre-scrubber: 0.144 (day 1) 0.033 (day 2)	R. Meij, pers. commun.
U.K.	Plant 1: 0.077 (THg) 0.0014 – 4.0 (diss. Hg) Plant 2: 0.010 – 0.022 (THg) 0.0067 – 0.020 (diss. Hg)	this study
Germany	Absorber (3 plants): 0.077 – 0.261 (diss. Hg) Pre-scrubber (3 plants): 0.152 – 0.318 (diss. Hg)	this study

THg = total mercury, diss. Hg = mercury in filtrate, Hg_s = mercury in solids

If the retention of mercury by wet scrubbers at power plants can be improved in the future, then it is likely that mercury concentrations in the scrubber liquids will increase. However, it is doubtful whether they will ever be high enough for the *BIOMER* process to be applicable. Consideration also has to be given to the fact that mercury is not the only contaminant in these waste waters. Microbial clean-up with the *BIOMER* process has proved its effectiveness in pilot-scale studies with wastewater from the chlorine industry [23] and is now in full-scale industrial operation at a Czech chlor-alkali electrolysis factory. In these wastewaters mercury is the main (if not the only) contaminant of concern. Effluents from wet scrubbers at coal-fired power plants on the other hand contain a multitude of other elements, apart from mercury, that require treatment before these waste waters can be discharged (Table 1). Therefore the existing wastewater treatment schedule (precipitation and pH adjustment, flocculation and coagulation) has to be employed by the plants, irrespective of whether there is any mercury in the wastewater or not.

3.2.2 Municipal waste incinerators

The *BIOMER* process could potentially find application in the waste incineration sector. Scrubber effluents from HCl-scrubbers in waste incinerators are characterized by low pH (~0.5) and high mercury and chloride concentrations. Some examples of mercury concentrations at different types of incinerators are given in Table 4. In the highly acidic pre-scrubbers, mercury is mostly present in dissolved form and is therefore available to bacteria. Treatability studies have already been carried out (section 4.2). However, other constituents (e.g. cadmium and lead) are also present in these effluents and require treatment (Table 2).

Table 4: Mercury concentrations found in scrubber effluents from waste incineration

Country	Hg, mg/l	Source
Germany	9	Experimental waste incineration plant TAMARA, Karlsruhe
Germany	49 460	industrial incinerator
Sweden	MercOx process: 0.4 – 500 (range) 20 – 30 (typical)	C.J. Löthgren, pers. commun.
Germany	HCl-scrubber: range 10 – 80 mg/L (filtrate) generally >95% in dissolved form	J. Böske, pers. commun.
Czech Republic	HCl-scrubber: 0.010 – 0.012* SO_2-scrubber: 0.0003	this study (samples provided by J. Reif)

* after addition of 'Sorbalit'

3.3 Cost comparison

3.3.1 Coal-fired power stations

A cost-comparison of the *BIOMER* process with other treatment technologies was not made, as

- no information was available on the operating costs of waste water treatment plants at coal-fired power stations;
- the *BIOMER* system would require significant scaling up due to the large wastewater volumes generated at power stations (typically 50 – 200 m^3/h), resulting in a significant increase in the associated investment costs;
- dissolved mercury concentrations in wastewater effluents from power plants are not high enough to warrant an application.

3.3.2 Municipal waste incinerators

Precipitation of heavy metals with trimercapto-s-triazine (TMT 15™) is a common wastewater treatment process at municipal waste incinerators, and is also used at some power stations. A cost comparison shows that the reagent costs for the *BIOMER* system are about EUR 0.19/m^3 treated wastewater, whereas the reagent costs for precipitation with TMT 15 are about EUR 1.56/m^3 (Table 5).

Table 5: Comparison of reagent costs for precipitation with TMT 15 vs. the *BIOMER* System

TMT 15	BIOMER
Dosing rate: 500 ml / m³ water	Sugar 100 g/m³
2.79 €/kg	0.5 €/kg → 0.05 €/m³
→1.56 € / m³ wastewater	Yeast Extract 20 g/m³
	7 €/kg → 0,14 €/m³
	→ 0.19 €/ m³ wastewater

The estimated investment costs for a *BIOMER* System capable of dealing with a wastewater throughput of up to 8 m^3/h or 70,000 m^3/y are on the order of EUR 500,000 [24].

An estimation of the annual operating and disposal costs for treatment with TMT 15 vs. the BIOMER process was made for the example of a Waste Fired Power Station in Ludwigshafen, Germany (Fig. 9).

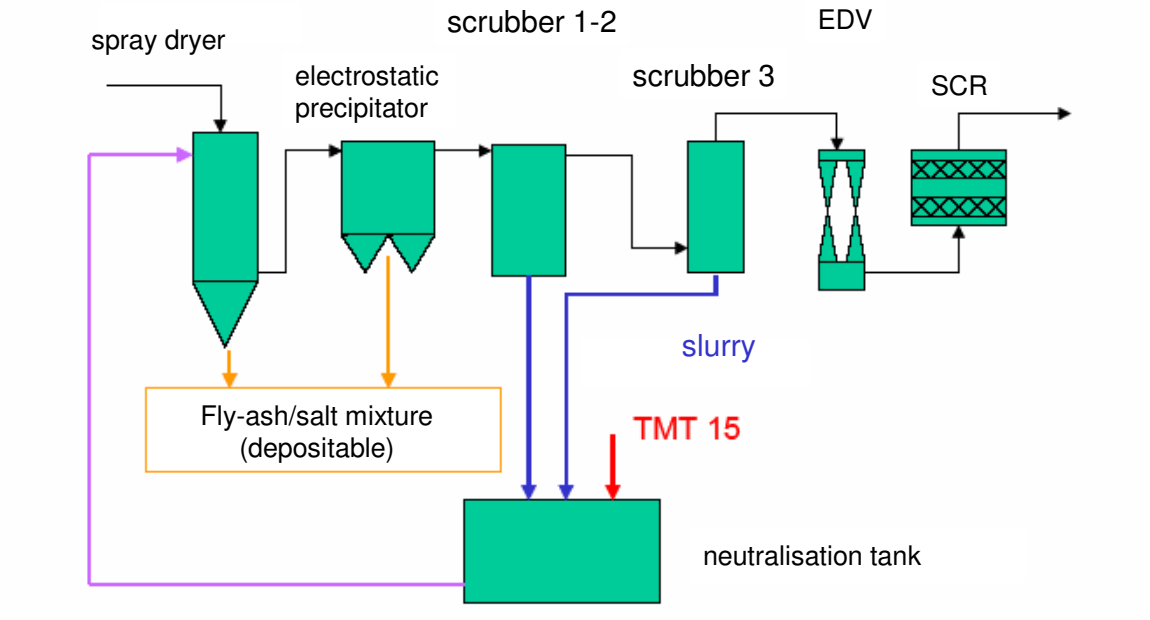


Fig. 9: Example of a Flue Gas Cleaning Line in a Waste Fired Power Station in Ludwigshafen (Germany)

Table 6: Comparison of estimated annual operating and disposal costs

TMT 15	BIOMER
Water: 775 l/h	Water: 775 l/h
Doses: 0.5 l/h	Doses sugar: 100 g/m³
Density: 1.12 kg/l	Costs sugar: 0.5 €/kg
Costs: 2.79 €/kg	Doses yeast extract: 20 g/m³
	Costs yeast: 7 €/kg
TMT 15 Costs: 10,937 €/a (7000 operation hours)	**Sugar / yeast: 1004 €/a** (7000 operation hours)
Disposal fly ash / salt: 2252 t	Biomass (Hg contaminated): 2.3 t/a (Hg content 3%)
Costs: 140 €/t	Costs: 300 €/t
Disposal Costs: 315,280 €/a	**Disposal Costs: 690 €/a***
Sum of Costs: 326,217 €/a	**Sum of costs: 1,694 €/a**

*Plus costs for the disposal of fly ash / salt

The yearly operating costs for treating a volume of 775 l/h (7000 operation hours) including disposal costs for the Hg contaminated biomass were only EUR 1,694/a for *BIOMER* compared to EUR 10,937/a for TMT 15 (Table 6). However, both of these costs were small in relation to the estimated disposal costs of EUR 315,000/a for the disposal of the fly ash / salt mixture which arises from the spray dryer and ESP used at the plant. Therefore the *BIOMER* process is not really viable for a plant with the above configuration.

The *BIOMER* process produces a mercury-contaminated sludge (Hg content 3%) which must be stabilised before disposal (unless it is disposed of as toxic sludge). However, the total amount of sludge produced is very small and is only 2.3 t/a in the above example. Depending on the concentrations of other constituents in the wastewater that require treatment, the application of *BIOMER* could potentially result in a reduction of the total amount of waste that has to be disposed of. In this context it is worth remembering that the Waste Incineration Directive [9] stipulates that residues from combustion processes must be minimised in their amount and harmfulness and recycled where appropriate.

4. Treatability studies

4.1 Coal-fired power stations

No treatability studies have been carried out on wastewater effluents from the power industry, as the dissolved mercury concentrations were found to be too low to make the process feasible.

4.2 Municipal waste incinerators

Treatability studies were carried out at GBF using incinerator samples obtained from the TAMARA test facility at the Research Center Karlsruhe [25]. Samples were taken from the first scrubber where the operating pH is less than 1.

Operation of the BIOMER System

A three step system was employed consisting of a bioreactor (1), a sand filter (2), and an activated carbon polishing filter (3). The working volume was 160 ml. Two kinds of activated carbon were used: 2/3 of size 3 mm and 1/3 of size <1 mm. The scrubber wastewater was neutralized, saturated with oxygen, and enriched with nutrients (0.1 g/l sucrose, 0.02 g/l yeast extract). The bioreactor was inoculated with 7 different microbial strains.

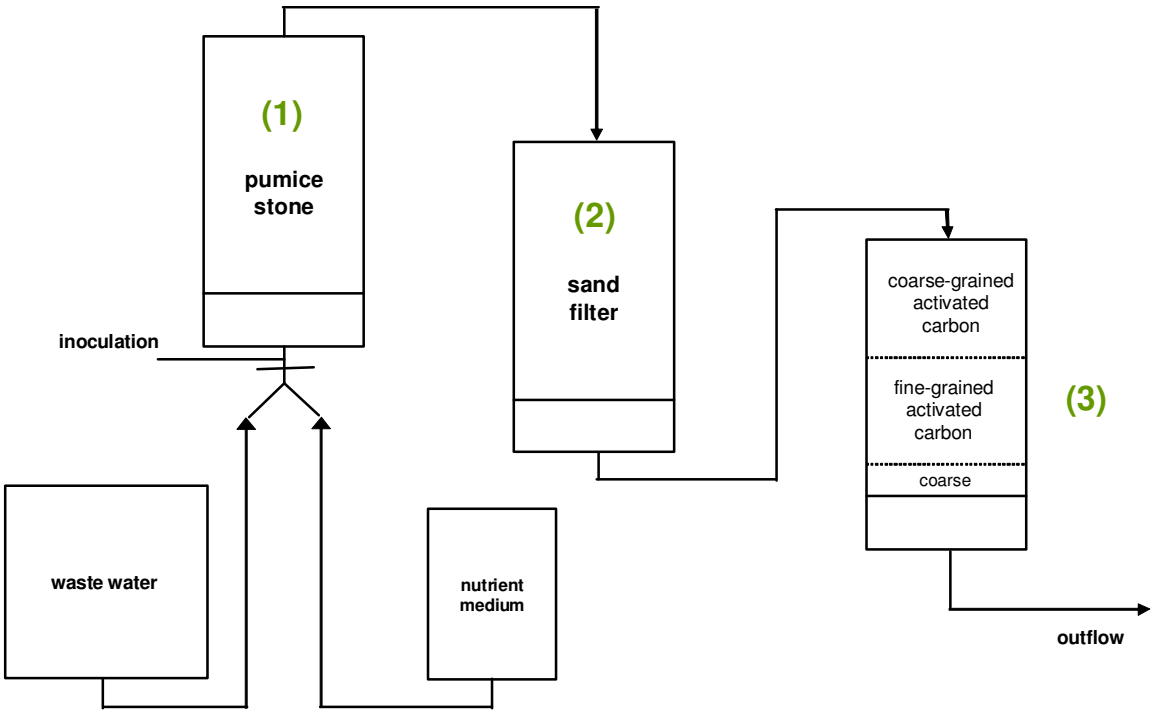


Fig. 10: Set Up of the *BIOMER* System

Wastewater parameters

- Wastewater pH of 0.3
- Mercury Concentration: 9 mg/l
- Chloride Concentration: 39 g/l
- Conductivity: 81 mS

Neutralization with 5 L of 10 M NaOH led to a yellow – brown precipitate (possibly consisting of Fe-hydroxides) that was sedimented and was not treated.

The experiment was conducted at three different inflow concentrations of mercury: 3 mg/l, 6 mg/l, and 9 mg/l.

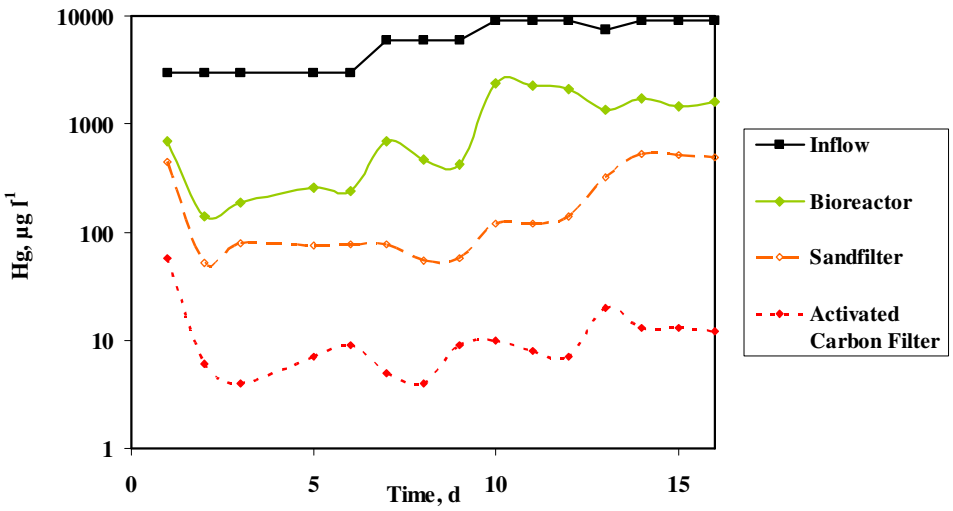


Fig. 11: Outflow concentrations of mercury for the three stages of the *BIOMER* treatment process

Results of treatability tests

The results of the treatability studies carried out with scrubber solutions from the incinerator indicated a high reduction efficiency of the bioreactor (92%) up to inflow concentrations of 6 mg Hg/l and 26 g chloride/l. At an inflow concentration of 9 mg Hg/l, the efficiency of the bioreactor was at first slightly lower due to the higher chloride content of 39 g/l, but efficiency could be increased by longer adaptation of the bacteria. Overall, the system worked well and the sand filter was able to reduce Hg concentrations further. Other experiments showed that a mercury concentration of up to 10 mg/l results in a bioreactor outflow of >500 µg/l. However, the system was found to be robust even at Hg outflow concentrations from the bioreactor of 2 mg/l which were reduced by the sand filter to 0.5 mg/l. The activated carbon filter had a stable outflow of 10-20 µg/l, which is well below legal discharge limits.

Conclusion from treatability tests

Scrubber effluents from waste incinerators are, in principle, treatable by the *BIOMER* process and this has been shown for a variety of Hg inflow concentrations. However, since other contaminants are also present in these effluents, the *BIOMER* process alone would not be sufficient and would have to be incorporated into a wider treatment train that is capable of dealing with all pollutants occurring in these waste waters.

5. Pilot operation or final remediation

Not applicable to Case Study 4.

6. References

[1] Utility Air Toxics Report to Congress, 1998
http://www.epa.gov/ttn/atw/combust/utiltox/utilfs.pdf

[2] Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Official Journal of the European Communities, L331/1-5, 15.12.2001.

[3] Pacyna EG, Pacyna JM (2002) Global emission of mercury from anthropogenic sources in 1995. Water Air Soil Pollut. 137 (1-4): 149-165.

[4] Mercury Study Report to Congress, 1997 http://www.epa.gov/mercury/report.htm

[5] UNEP (United Nations Environment Programme). Global Mercury Assessment Report. UNEP Chemicals, Geneva, Switzerland, December 2002.
http://www.chem.unep.ch/mercury/

[6] EPRI 2004, quoted in: Update - Clean Air Mercury Rule (CAMR). Presentation to Clean Air Act Advisory Committee by Sally L. Shaver, Emission Standards Division, Office of Air and Radiation, June 24, 2004.

[7] EU Mercury Strategy http://ec.europa.eu/environment/chemicals/mercury/index.htm

[8] Clean Air Mercury Rule (CAMR) http://www.epa.gov/air/mercuryrule/

[9] Large Combustion Plants Directive (LCPD, 2001/80/EC)
http://europa.eu.int/eur-lex/pri/en/oj/dat/2001/l_309/l_30920011127en00010021.pdf

[10] DTI, 2003. Flue Gas Desulphurisation (FGD) Technologies for Coal-Fired Combustion Plant. Report CB013, Department of Trade and Industry, March 2003.

[11] Adams DMB, Fernando R, 1998. Coal-fired power station effluents. Technical Report CCC/10, IEA Coal Research, London, November 1998.

[12] Reference Document on the Best Available Techniques for Large Combustion Plants. European IPPC Bureau, May 2005.

[13] Hein et al., 2002. Quecksilber und seine Verbindungen bei der Abfallverbrennung. Institut für Verfahrenstechnik und Dampfkesselwesen, Universität Stuttgart, Dezember 2002.

[14] Meij R, Vredenbregt LHJ, Winkel HT. The fate and behavior of mercury in coal-fired power plants. J. Air & Waste Manage. Assoc. 52 (8): 912-917, 2002.

[15] Assessment of Control Options for Mercury. BIOMERCURY Project Report, Deliverable D14, March 2006. Available at http://biomercury.de/

[16] Achternbosch M, Richers U, 2002. Material Flows and Investment Costs of Flue Gas Cleaning Systems of Municipal Solid Waste Incinerators. Forschungszentrum Karlsruhe, Wissenschaftliche Berichte FZKA 6726.

[17] European Pollutant Emission Register (EPER) http://eper.ec.europa.eu/

[18] Directive on Integrated Pollution Prevention and Control (IPPC, 96/61/EC) http://europa.eu.int/comm/environment/ippc/

[19] Directive 2000/76/EC on the incineration of waste http://europa.eu.int/comm/environment/wasteinc/newdir/2000-76_en.pdf

[20] Chang JCS, Ghorishi SB. Simulation and Evaluation of Elemental Mercury Concentration Increase in Flue Gas Across a Wet Scrubber. Environ. Sci. Technol., 37 (24), 5763 -5766, 2003

[21] Achternbosch M, Richers U, 1996. Stoffstromanalysen zur abwasserfreien und abwassererzeugenden Verfahrenskonzeption von "nassen" Rauchgasreinigungs-systemen. Forschungszentrum Karlsruhe, Wissenschaftliche Berichte FZKA 5773.

[22] Gutberlet H, 1984. Measurement of Heavy Metal Removal by a Flue Gas Desulfurization Plant working by the Lime Scrubbing Method. Research Report ENV – 492 – D (B), VEBA Kraftwerke Ruhr AG, Gelsenkirchen.

[23] Wagner-Döbler I. (2003) Pilot plant for bioremediation of mercury-containing industrial wastewater. Appl. Microbiol and Biotechnol. 62 (2-3): 124-133.

[24] Data from J. Leonhäuser, GBF

[25] Leonhäuser J, Korell J, Paur HR, Wagner-Döbler I. Results of Treatability Studies on Scrubber Solution from Municipal Waste Incinerators. Presentation at BIOMERCURY Project Meeting, 11 December 2004, University of Lodz.

7. Appendices

Appendix A

Determination of mercury concentrations in process water samples obtained from two coal-fired power stations in the U.K.

Sample description

U.K. Power Station 1

Set 1A
A set of 2 duplicate samples (2 x 100 ml) was taken at 11:30 a.m. on 5 consecutive days (28/11/2005-02/12/2005) from the waste equalisation tank (WWTP Equalisation Tank 1). This tank is located between the hydrocyclones and the wastewater treatment plant (WWTP) and is open to air. It is the earliest point after the absorber that can be sampled, with the exception of point B below.
All samples were preserved with 0.5% HCl. Five samples were sent to GBF for analysis. Duplicate samples were analysed by SOTON for QC purposes.

1B
One sample (500 ml) was taken on 05/12/2005 from the pH control tank before the hydrocyclones. This is the earliest point after the absorber that can be sampled.
The sample was preserved with 0.5% HCl. One 100 ml subsample was sent to GBF for analysis. Duplicate samples were analysed by SOTON for QC purposes.

U.K. Power Station 2

Set 2A
A set of 5 samples (one per day) were taken on 5 consecutive days (28/11/2005-02/12/2005) of the supernatant liquid from the dewatering tank (i.e. the supernatant from the settled gypsum slurry that comes from the absorber unit). The dewatering tank is the earliest point after the absorber that can be sampled.
All samples were preserved with 1% HCl. Four samples were sent to GBF for analysis. One sample was analysed by SOTON.

Set 2B
A set of 5 samples (one per day) were taken on 5 consecutive days (28/11/2005-02/12/2005) 1from the first reaction tank in the wastewater treatment plant (WWTP). This is the input to the WWTP, before any chemicals are added.
All samples were preserved with 1% HCl. Four samples were sent to GBF for analysis. One sample was analysed by SOTON.

Analysis

SOTON set up new analytical facilities for mercury determination in January 2006. Power station samples were analysed in February 2006 following completion of setup and method validation.

Determination of total mercury content in the liquid phase

40 ml aliquots of the supernatant liquid from the process water samples were oxidised with 7.5 ml of 33% v/v HCl and 1 ml 0.1N $KBr/KBrO_3$ reagent. Samples were diluted to 50 ml with Milli-Q water and the closed vessels were allowed to stand overnight for complete digestion. Just before analysis, the samples were pre-reduced with 15 µl of 12% m/v hydroxylamine hydrochloride to destroy excess bromine. Total Hg was determined on a continuous flow CV-AFS system (Millenium Merlin 10.025, PS Analytical, Kent) after $SnCl_2$ reduction, using high purity argon (99.99%) as the carrier gas.
Quality control included daily instrument calibration, duplicate analyses, matrix spikes and analysis of blank samples. The method detection limit was 5 ng/L.

Determination of total mercury content in the solid phase

Process water samples from Power Station 1 were filtered through Whatman 541 filter paper (pore size 20-25 µm). The deposit on the filter paper was air dried to constant weight and placed in a desiccator. 0.1 g portions of the dried sludge were weighed into borosilicate tubes and were digested in closed vessels with 1.5 ml of 36% m/m HCl and 0.5 ml of 70% m/m HNO_3 at 140°C for 20 mins. The digest was diluted with 1 ml Milli-Q water and heated for another 10 mins. The tubes were allowed to cool and samples were diluted with Milli-Q water to 100 ml and filtered through a Whatman 541 filter paper. 10 ml aliquots of the filtered aqua regia extract were analysed by CV-AFS (Millenium Merlin 10.025, PS Analytical, Kent) after $SnCl_2$ reduction.

Results

The analytical results obtained by SOTON are detailed in the tables below. For power station 1, Hg concentrations in the liquid phase ranged from 22.4 to 29.0 µg/L (mean 25.3 µg/L) and were thus lower than those determined by GBF (47-61 µg/L, mean 54 µg/L). The maximum Hg concentration determined in the liquid phase of samples obtained from power station 2 was 13.8 µg/L (GBF measured 10-20 µg/L).

U.K. Power Station 1

Sample code	Hg in liquid (µg/L)	Hg in solids (mg/kg)
Set 1A		
1A-2	24.71	9.01
1A-4	28.95	10.67
1A-6	22.35	11.17
1A-8	24.47	6.98
1A-10	25.76	6.72
1B		
1B-1	1.99 / 1.42 / 2.90	2.28

U.K. Power Station 2

Sample code	Hg in liquid (µg/L)	Hg in solids (mg/kg)
2A-5	13.8 / 6.66	not determined*
2B-5	4.18 / 0.39	not determined*

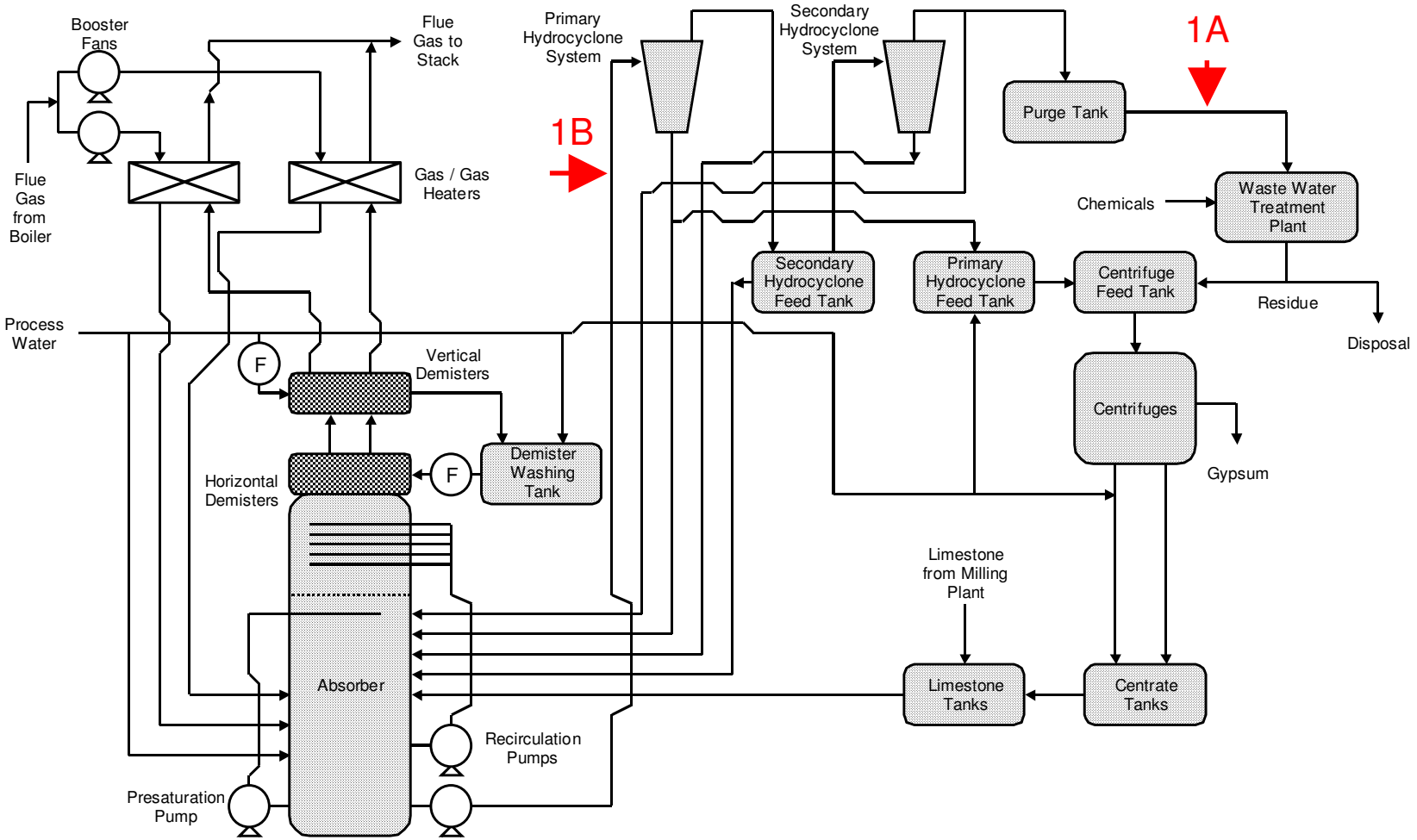
*insufficient material for analysis

It is interesting to note that for power station 1, Hg concentrations are higher in the samples taken from the waste equalisation tank than in the samples taken directly after the absorber stage. A possible explanation may be changes in physical (pH, redox) and/or chemical conditions and associated desorption of Hg from particulates.

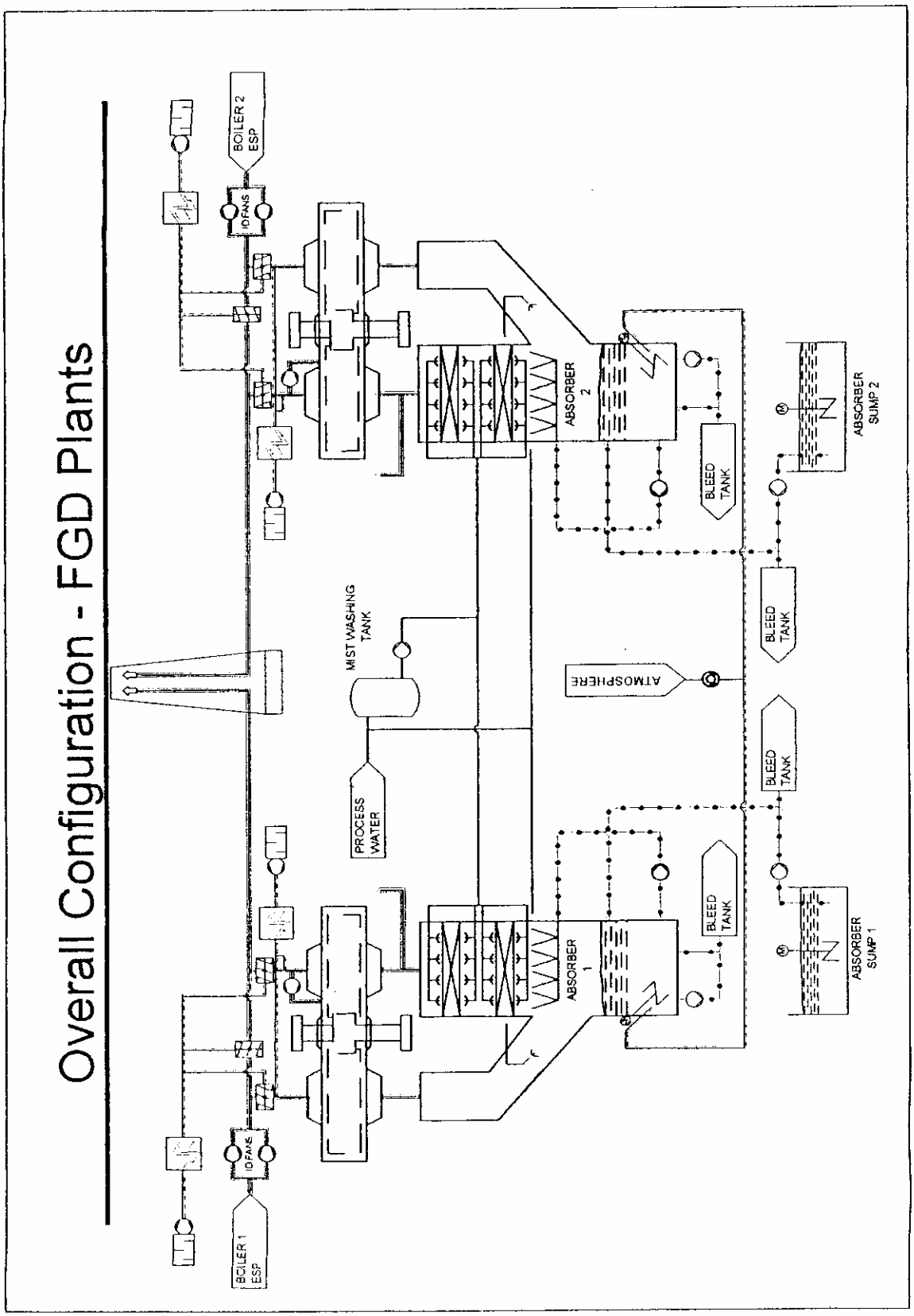
Conclusions

The measured concentrations are too low for treatability studies by the *BIOMER* process. Further efforts should therefore focus on obtaining samples from power plants operating with a pre-scrubber, where higher Hg concentrations may be present.

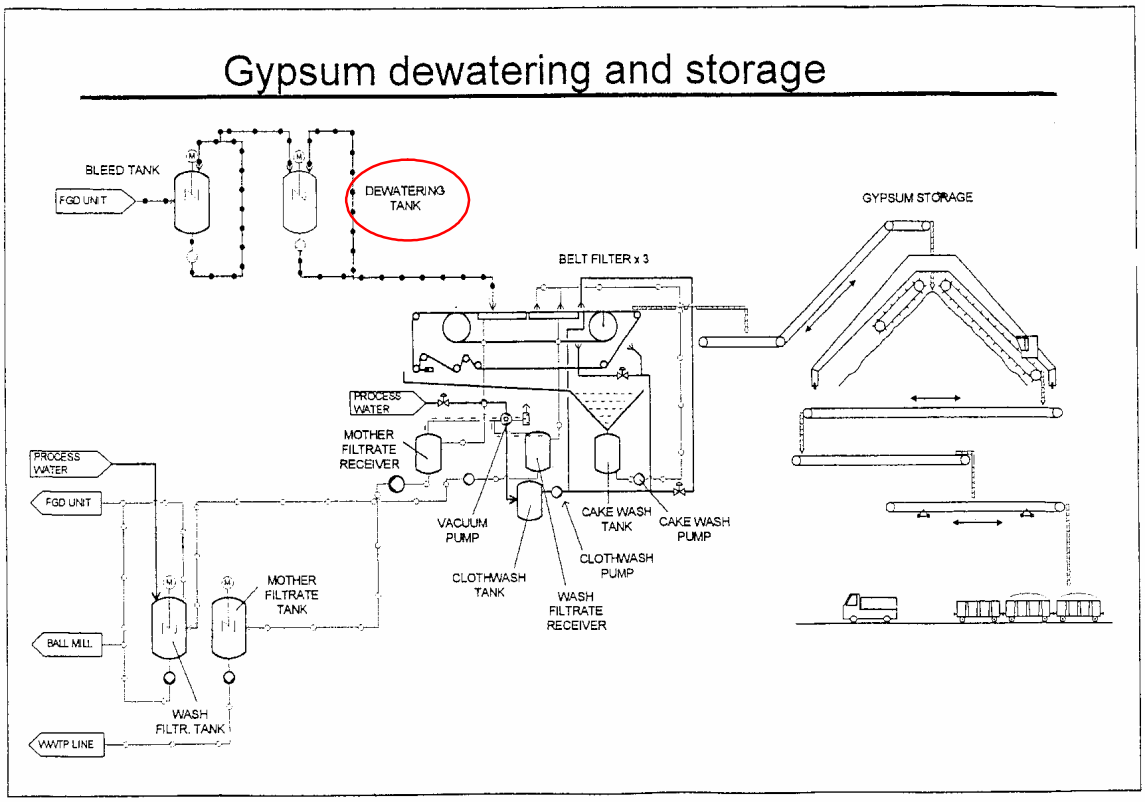
Overall FGD Process Scheme and Sampling Points, Plant 1:



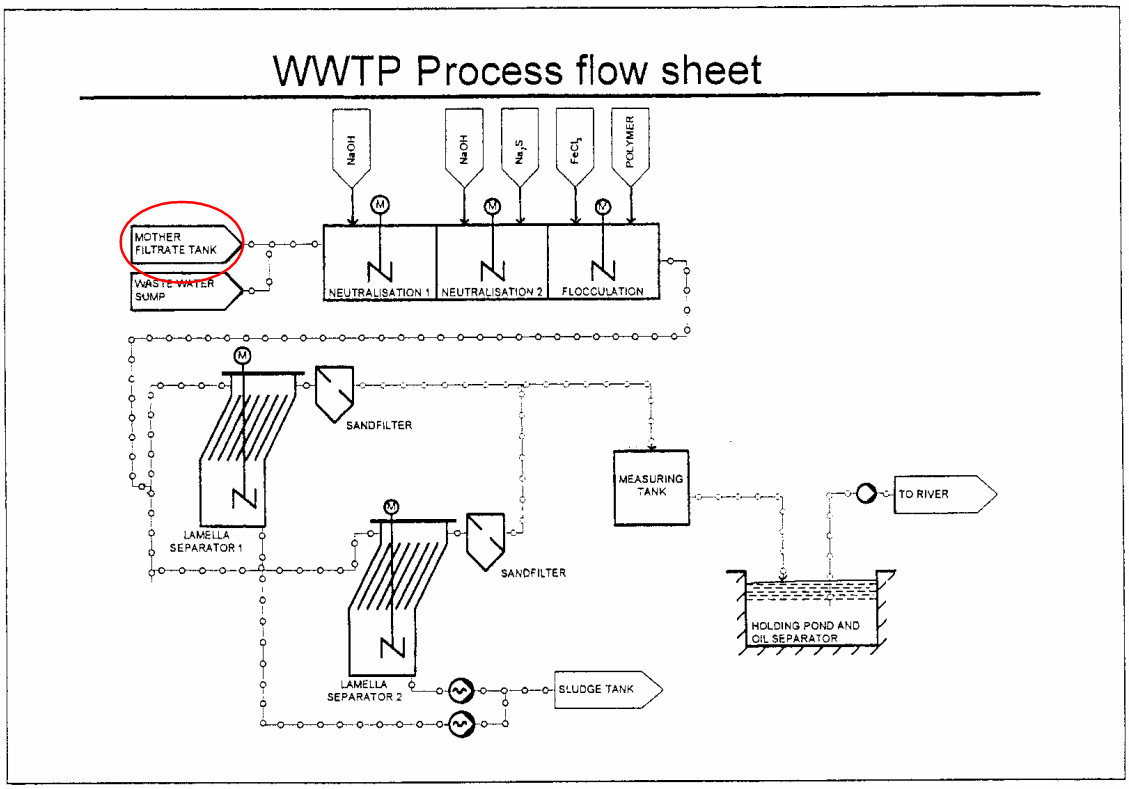
Overall FGD Process Scheme, Plant 2:



Plant 2, Sampling point 1:



Plant 2, Sampling point 2:



Appendix B

Determination of mercury concentrations in process water samples obtained from a coal-fired power station in Germany and from a municipal waste incinerator in the Czech Republic

Sample description

Power Station Samples

Three sets of two duplicate samples (2 x 500 ml) were taken on 26 October 2006 from three different types of scrubber/pre-scrubber configurations at a German coal-fired power station. The redox potential registered in the absorbers at the time of sampling ranged between 260 and 600 mV, and the pH between 5.2 and 5.5. The pH in the pre-scrubber samples ranged from 1.2 to 1.6.

Incinerator samples

Two samples were received from a waste incinerator in Prague, one was taken from the pre-scrubber (pH <1) and one from the main scrubber operating at pH 6.

Analysis

The samples were analysed in November 2006, within 7 – 10 days of receipt in SOTON's laboratory.

Determination of total mercury content in the liquid phase

40 ml aliquots of the supernatant liquid from the process water samples were oxidised with 7.5 ml of 33% v/v HCl and 1 ml 0.1N $KBr/KBrO_3$ reagent. Samples were diluted to 50 ml with Milli-Q water and the closed vessels were allowed to stand overnight for complete digestion. Just before analysis, the samples were pre-reduced with 15 µl of 12% m/v hydroxylamine hydrochloride to destroy excess bromine. Total Hg was determined on a continuous flow CV-AFS system (Millenium Merlin 10.025, PS Analytical, Kent) after $SnCl_2$ reduction, using high purity argon (99.99%) as the carrier gas.
Quality control included daily instrument calibration, duplicate analyses, and analysis of blank samples. The method detection limit was 5 ng/L.

Determination of total mercury content in the solid phase

Process water samples were filtered through Whatman 541 filter paper (pore size 20-25 µm). The deposit on the filter paper was air dried to constant weight and placed in a desiccator. 0.1 g portions of the dried sludge were weighed into borosilicate tubes and were digested in closed vessels with 1.5 ml of 36% m/m HCl and 0.5 ml of 70% m/m HNO_3 at 140°C for 20 mins. The digest was diluted with 1 ml Milli-Q water and heated for another 10 mins. The tubes were allowed to cool and samples were diluted with Milli-Q water to 100 ml and filtered through Whatman 541 filter paper. 10 ml aliquots of the filtered aqua regia extract were analysed by CV-AFS (Millenium Merlin 10.025, PS Analytical, Kent) after $SnCl_2$ reduction.

Results and discussion

The analytical results obtained are detailed in the two tables below.

Power Station Samples

Sample code		Hg in liquid (µg/L)	Hg in solids (mg/kg)
Set 1	1V1	203	37.1
	1V2	197	69.5
	1A1	270	0.280
	1A2	252	0.369
Set 2	2V1	318	11.8
	2V2	318	9.61
	2A1	240	1.01
	2A2	250	3.28
Set 3	3V1	145	7.89
	3V2	158	12.0
	3A1	78	0.768
	3A2	76	1.25

In the sample code, 'V' denotes samples taken from pre-scrubbers, whereas 'A' are absorber samples. All of the measured concentrations are a lot higher than those determined in samples from power stations in the U.K. (surprisingly, even the absorber samples had quite high levels in comparison with the U.K. samples). However, the mercury concentrations do not seem to be high enough for the *BIOMER* technology to be applicable. Also, a large proportion of the mercury in the pre-scrubber effluents appears to be solid-bound and would not be immediately accessible to microorganisms. The variability between the three sample sets is also quite large, reflecting the fact that the Hg chemistry and partitioning behaviour is very much influenced by the characteristics of the coal feed and the operating conditions of the air pollution control equipment.

Incinerator samples

Sample code	Hg in liquid (µg/L)	Hg in solids (mg/kg)
WI-PRE	10.1 / 12.0	1409
WI-MAIN	0.30	0.80

Dissolved mercury concentrations in the pre-scrubber effluents obtained from the Czech waste incineration plant were unexpectedly low. The reason became apparent on an examination of the mercury content in the solid phase: almost all mercury was solid bound (1.4 g/kg). We found that this incinerator uses lime with up to 10% of activated carbon (trade name 'Sorbalit'), and this absorbent seems to be added directly to the pre-scrubber. The transfer of mercury to the main scrubber is also very low. Therefore the *BIOMER* process would not be applicable at this particular plant.

Power Station Samples taken in October 2006

SPECIFIC SUPPORT ACTION

BIOMERCURY

Worldwide remediation of mercury hazards through biotechnology

NMP2-CT-2004-505561

Priority 3 NMP: Nanotechnology and nanosciences, knowledge based multifunctional materials, new production processes and devices

Deliverable 20

Case study: Mercury in gas and oil industry

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1. Introduction

The production of natural gas is normally associated with a number of contaminants such as CO_2, H_2S, and others. Mercury also represents serious problems in many of the natural gas wells. Mercury is harmful to man and ecosystems and also represents technological risk due to corrosive effects in installations. Numerous reported cases all over the world (USA, Algiers, Indonesia) describe huge failures resulting with damages and environmental catastrophes as a consequence of uncontrolled presence of mercury in gas. Removal of mercury in natural gas production facility is therefore mandatory.

Most if not all mercury in natural gas is present in elemental form and no natural gas processing plant problems are suspected to have been caused by organic and inorganic mercury compounds. Elemental mercury is the main cause of mercury corrosion problems. Moreover, trace quantities of H_2S, very often present in the natural gas, are the catalysts for the reaction of mercury with iron oxide from the pipe, vessel or reactors. Although the concentration of mercury in a given natural gas may be considered very low, its effects are cumulative as it amalgamates. Elemental mercury forms an amalgam with the surface layer of the metal it contacts. To date, the most serious problem reported by the industry owing to mercury corrosion has been the result of mercury forming an alloy with aluminium (amalgam). To initiate aluminium corrosion, the tightly adhered Al oxide layer on the surface of the aluminium must be removed. The mercury/aluminium amalgam removes this layer. Aluminium is a predominant choice in cryogenic services due to its excellent properties. In order to avoid problems due to the presence of mercury, mercury MUST be completely removed to no detectable levels in upstream equipment. The most frequently applied procedure to remove mercury as an impurity is based on adsorption of Hg on activated (sulphur impregnated) carbon.

Mercury in gas condensates may occur in a wide concentration ranges (10 to 3000 ng/ml). The prerequisite of risk assessment is the accurate measurements of its concentration, its distribution among the various distillation fractions and its distribution among various chemical forms. Whereas the distribution of mercury in crude petroleum

and gas condensates are well known, the forms of mercury compounds present are uncertain (Wilhelm and Bloom, 2000). Mercury in the gas condensate is present in a variety of physical and chemical species that feature different solubility, volatility, toxicity and chemical reactivity (Frech et al., a, b, 1996).

The determination of mercury speciation among different defined chemical species in a system in feedstock supply and refinery products is essential to understand the mechanisms of the interaction of mercury with equipment, catalysts and mercury removal technology, and to evaluate the potential hazard to maintenance workers.

Speciation of mercury in gas condensates and other petroleum samples is difficult because of the wide range of boiling points, the complexity of the condensate matrix and the similarity of its physicochemical properties. In most cases the speciation was operationally defined by the use of sequential extractions followed by the determination of total mercury in subsequent fractions (Frech et al. a,b, 1996). Species selective methods were further developed and applied by a number of authors using chromatographic methods with element specific detectors (Snell et al., 1996; Tao et al., 1998; Shafawi et al., 1996, Bouyssiere et al., 2002).

Sampling of gas condensates for mercury speciation analysis is a critical step of analytical procedure and is potentially a source of considerable errors. Significant losses of mercury and changes in its speciation may occur by reaction of species with atmosphere and sample container material, and by reactions between the species and the gas condensate constituents. Therefore a condensate sample should be taken directly from the feed liquid previous to contact with air and water. Preferably, the analysis should be done on site, or, if not feasible, the sample should be transferred into a glass- of Teflon-lined container without a headspace and the time between sampling and analysis should be reduced to a minimum.

1. Containers: Hg(II) may be lost within 3 days, probably by sorption, whereas the Hg(0) may be lost within 30 days. Other materials such as plastics Hg(0) may be lost due to diffusion through the container wall. Hg(II) is rapidly lost from almost all containers, except those made of aluminium (Bloom, 2000).
2. Species inter-conversion: Chemical reactions between $HgCl_2$ and Ph_2Hg and between MeHgCl and Ph_2Hg take place. Another, very important reaction

leading to analytical error is the formation of Hg(I) compounds from the dissolved Hg(0) and $HgCl_2$. When these tow forms are present at the same time , Hg_2Cl_2 is formed and precipitated as a colloid and is not soluble in organic solvents.

The deliverable 20 deals with mercury data obtained in natural gas production facilities at Molve, Croatia and oil refinery Novi Sad, Serbia and Montenegro. The main aim was to investigate whether during such a process wastes from Natural gas treatment facilities and oil refineries contain mercury at concentrations and forms that will allow the removal of mercury using bioremediation technology investigated/promoted in the framework of the biomercury project.

2. Experimental

Sampling was conducted at the Ina naftaplin natural gas treatment facilities at Molve, Croatia, while samples from an oil refinery were obtained from Novi sad, Serbia and Montenegro.

2.1. Sampling:

a) Sampling at the Natural Gas Treatment Facility, MOLVE, Croatia, was performed in May 2005. The facilities (Figure 1) are located about 100 km northeast from Zagreb. Liquid samples were taken directly from feed liquids leaving no headspace in 1000 ml Teflon and Pyrex glass containers. Each sample was taken in two 1000 ml bottles. In addition, activated carbon samples used for the removal of mercury were also taken for analysis. Samples were then transported to the laboratories of the Jozef Stefan Institute in Ljubljana.

Liquid samples were stored in refrigerator until further analysis. Activated carbon samples were crushed and ground in a zirconium mortar with Zr ball in a Fritch vibration micro-pulverizer. During homogenization special care was taken to avoid cross contamination of samples.

b) Sampling at oil refinery Novi sad:

Sampling was performed in May 2006 by GEOTEST. Most samples were collected into glass containers and emulsions were stored in plastics.

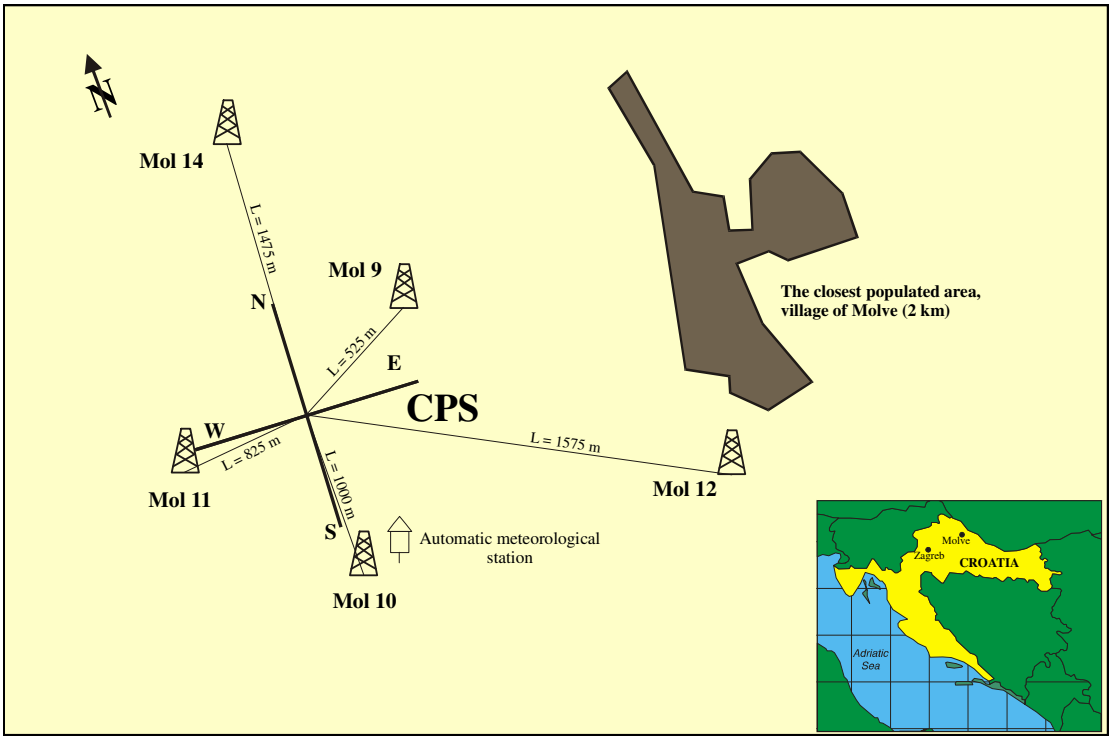

Figure 1. Study area Molve: natural gas wells and facilities for processing (CPS: Central Processing Station)

2.2. Analytical methods

Total mercury analysis in water

About 100 ml of sample was transferred directly in a Teflon bottle, and after addition of 0,5 ml of conc. HCl and 1 ml of BrCl, the bottle was closed and the mixture was left to react at the room temperature under UV light for three hours. 60µl of 12% solution of $NH_2OH \cdot HCl$ was added just before the analyses and an aliquot of the digest was than added to the reduction cell. After reduction with $SnCl_2$ mercury was swept from the solution by aeration and concentrated on a gold trap. Mercury was then released from

the gold trap by heating and measured on an LDC Milton Roy instrument by cold vapour atomic absorption spectrophotometry (CV AAS). A detailed description of the methods is elsewhere (US EPA 1631). The detection limit of the procedure is 0,2 ng/L. (Horvat et al., 1986, 1991, 1993). The reproducibility of the method is 5 to 10%. Estimated uncertainty with a coverage factor k=2 was 6.3%. During each batch of sample analysis 2 reagent blank plus the sample processing blank were also analysed in order to avoid uncontrolled contamination. In the case of the analysis of such high Hg concentrations, reagent blanks were negligible.

Total mercury analysis by thermal decomposition of samples

Two approaches were used, the first was laboratory build, simple method, and the second was a commercially available DMA-80 method.

a) The first was a simple laboratory build system based on thermal decomposition for the one step determination of mercury (Liang et al., 2000). Samples were directly introduced into the thermal decomposition system without prior preparation. The combustion was conducted at about 800°C for a period of 4 min, with continuous flow of air. Mercury evaporated from the sample was carried with the flow of air through an aqueous wash bottle and soda lime traps and then trapped onto the gold trap. The gold sand trap was then heated to release elemental mercury to the AFS detector. The system was calibrated by working calibration aqueous solutions.

b) Commercially available DMA-80 Direct Mercury Analyzer (Milestones) was used. Solid or liquid samples are weighed and introduced into the sample boat. The sample is initially dried in an oxygen stream passing through a quartz tube located inside a controlled heating coil and then thermally decomposed in a continuous flow of oxygen. The combustion gases are carried off and further decomposed on a catalytic column at 750 °C. Mercury vapors are trapped on a gold amalgamator and subsequently desorbed for quantitation. The mercury content is determined using atomic absorption spectrophotometry at 254 nm.

Determination of total mercury in gas condensates at GBF

These samples were also analysed by the GBF. For the measurement of total mercury the *aqua regia* digestion was done. Hereby a 50 ml flask was filled with 1 ml (0.67 g) condensate sample, 21 ml HCl (37%) and 7 ml HNO_3 (65%). After heating the suspension 2 hours at 95°C in water bath the sample was cooled down and filled up with 3% HNO_3 up to 50 ml. The sample was filtered with a filter paper and a sub-sample was measured at the AAS whereby $NaBH_4$ as reducing agent was used.

Determination of methylmercury (MeHg) by acid dissolution/solvent extraction/aqueous phase etylation/isothermal GC/CV AFS detection

Approximately 30 ml of sample was weighed directly in a 125 mL Teflon bottle and diluted up to 70 mL. After addition of 5 mL of conc. HCl and 30 mL of CH_2Cl_2, the bottles were closed and shaken over night. Water phase was then removed with water pump and approximately 40 mL of Milli-Q water was added to the CH_2Cl_2. Organic phase was evaporated on water bath at about 90°C. Samples were then purged with N_2 for 5 minutes to remove remaining CH_2Cl_2. This extraction was repeated twice. An aliquot of the aqueous sample was added to Teflon reaction vial and pH was adjusted to be 4.6 with addition of 100 µL of acetate buffer. 50 µL of 1% $NaBEt_4$ was added in the reaction vial at the end and the mixture was left to react at the room temperature for 15 minutes. Ethylated MeHg as ethylmethylmercury was purged onto Tenax trap for 15 minutes with Hg-free nitrogen. Tenax traps were then connected to the flow of argon and MeHg was thermally desorbed (180°C) onto isothermal GC column. Hg species were converted to Hg^0 by pyrolysis at 600°C and measured by cold vapour atomic fluorescence detector (CVAFS). The limit of detection, calculated on basis of three standard deviations of blanks, was about 10 pg MeHg/L. (Horvat et al., 1993).

The reproducibility of the method is 5 to 10%. Estimated uncertainty with a coverage factor k=2 was 4 %.

Recovery of MeHg was estimated by spiking the samples with known amount of MeHg prior extraction and analysis and have shown to be between 86% and 94%, therefore the

mean recovery factor (90%) was used in the calculation of the results. During each batch of sample analysis 2 blanks (reagent blank plus the sample processing blank).

Determination of total mercury by NAA

K0-INAA: Powdered well homogenized solid samples (about 150 mg) were sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). Samples and standards (Al-0.1%Au IRMM-530 disc of 6 mm in diameter and 0.2 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 2 minutes in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the Jožef Stefan Institute at a thermal neutron flux of $1.1 \cdot 10^{12}$ cm^{-2} s^{-1} (Jaćimović, 2003, Jaćimović and Horvat, 2003). For peak area evaluation, the HyperLab (HyperLab 2002 System, 2002) program was used.

Radiochemical NAA: For the determination of Hg by RNAA, subsamples were sealed in quartz ampoules and irradiated for 16-20 h at the fluence rate above. The samples were pyrolyzed resulting in volatilization of the Hg and Se; Se was trapped on soda lime and Hg was trapped on Se-impregnated paper. The gamma activity of the isolated radionuclides was counted with a NaI(Tl) detector (Kosta and Byrne, 1969, Byrne and Kosta, 1973).

Both INAA methods are very convenient for determination of high concentrations of Hg, as the linearity range is very broad, therofore corrections for dilution factors are not needed.

Escka method for the determination of total mercury at very high concentrations

This gravimetrical method is useful for fast determination of high total mercury in ores and mineral samples and is based on the formation of amalgam on the gold cover. In this study it was used for the determination of total mercury in activated carbon samples. Well ground and dried sample is weighted into a porcelain crucible. Three grams of iron powder is added in order to bind sulfur which is formed ($HgS + Fe \rightarrow FeS + Hg$). The content is well mixed and then coved with a layer zinc oxide, which retains organic compounds present in the sample, which otherwise could evaporate and condense on the Au cover. The crucible is covered with a gold cover of known weight.

Mercury vapor should not escape from the crucible, therefore careful checking for possible leaks are necessary. The crucible is then heated in an oven at 600 – 800^{o}C for 30 min. The Au cover is adjusted to such a form to allow the addition of cold, demineralized water on the top. The temperature of the water needs to be changed several times, if needed. The temperature of the water should not exceed 40^{o}C. After heating, the crucible with the Au cover is carefully removed. When cooled the Au cover is cleaned from the outside of possible dust. Also from the inside any moisture on the surface needs to be removed by a filter paper. The cover is weighted again and from the difference the total Hg content is calculated. The maximum amount of Hg that can be determined is 60 mg of Hg. In case larger amounts are recorded, the analysis needs to be repeated with less sample intake

3. Results and discussion

3.1. Natural gas treatment facility, Molve

Samples from the Natural gas treatment facilities were collected at as many stations as possible, including different wells, such as Molve, Stari Kalinovac, Gola and Gradac. At the well source natural gas contains three phases, gas, condensate and water phase (including debris). Water phase is re-injected, while natural gas and condensate are separated in the three phase separator and subjected to further processing (Figure 2). Concetrations for total mercury are reported in Table 1. The concentrations of total mercury in gas phase is regularly monitored and varies from 20 to 50 µg/m^3, re-injected water including solid debris varies from < 1 µg to 80 µg/L (Špirić, 1998). During our sampling the value for total mercury was relatively low (0.4 µg/L). The liquid hydrocarbon phase (condensate) contains extremely high concentrations (900 – 1200 µg/kg) at most wells except at Gola and east well Molve, where the values are in the range between <1 µg/kg to 3 µg/kg. The total amount of condensate produced yearly is about 200.000 m^3/y.

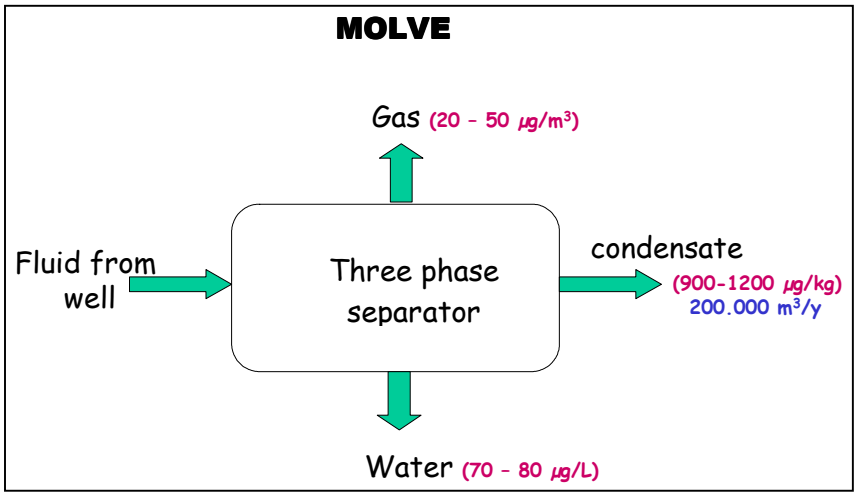

Figure 2. Three phase separator at the natural gas treatment facility.

Condensate is then further transferred and processed in oil refineries, while the gaseous phase (natural gas) is transferred to the central gas treatment facility. Firstly, the gaseous phase is washed in the water wash unit (Figure 3). Aqueous phase was sampled for total Hg measurements before and after washing and the values were 0,5 µg/L and 1,3 µg/L, respectively. This indicates that most of mercury in the natural gas is elemental Hg (Hg(0)), not soluble in water. Hg(0) from the natural gas is further carried through activated carbon traps, where Hg(0) is quantitatively adsorbed. The remaining Hg in gas is further removed in the process as shown in Figure 3. Final concentration of Hg in natural gas reaches values down to 5 to 10 ng/m3, which does not represent any technological and/or ecological problems.

Sampling of the condensate was done with use of Pyrex glass and Teflon bottles. Results in Table 1 clearly demonstrate that the both containers provided similar results for total Hg (i.e. no significant differences).

Mercury speciation was firstly done in re-injected water samples, in order to check for the presence of organic mercury. MeHg values are about 5 % of total Hg (Table 2). The well water sample taken for analysis was low in total mercury and we intended to repeat the measurements over the next sampling periods, especially due to the well known fact

that these values may reach as high as 70 - 80 µg/L of total mercury. This has not been done, due to the conclusions that this water is re-injected anyway, and would not be subjected to cleaning process. In case the aqueous phase would not be re-injected, further investigation of mercury speciation (especially the presence of Hg(II) and organomercury species would highly be recommended.

Table 1. Total mercury concentrations in various samples taken at Inanaftaplin Molve

Sample ID	**Total Hg, µg/kg**		**Mean µg/kg**
Sthal Molve	2,4	2,6	2,5
Water prior natural gas washing	0,5	0,4	0,4
Water after natural gas washing	1,3	1,4	1,3
Re-injected salted water	0,4	0,4	0,4
East well, Molve, Condenste	2,8	3,0	2,9
Molve condensate	46,7	44,7	45,7
Molve condensate - Gola	0,5	0,6	0,5
Mixed condensate– Pyrex glass	940	934	937
Mixed condensate– Teflon	1270	1210	1239
Condensate Kalinovac – Pyrex glass	972	1029,0	1000
Condensate Kalinovac - Teflon	1106	1294	1200
Stari gradac, Condesate – Pyrex glass	1207	1364	1286
Stari gradac, Condensate - Teflon	1083	1107	1095
Conostan oil, 11.8 ng/g (Reference material)	*11,5*	*11,6*	*11,6*

Table 2. Mercury speciation in desalter water sample

Sample	THg µg/L	Mean THg µg/L	MeHg ng/L	Mean MeHg ng/L
			2,78	
	0,041		2,79	
Desalter water	0,044	0,043 ± 0,002	2,09	2,55 ± 0,40
Water before washing	0.5 µg/L		<0,010	
			3.42,	
			2,79	
			3.66	
Water after washing	1.3 µg/L		3,86	3,43 ± 0,46

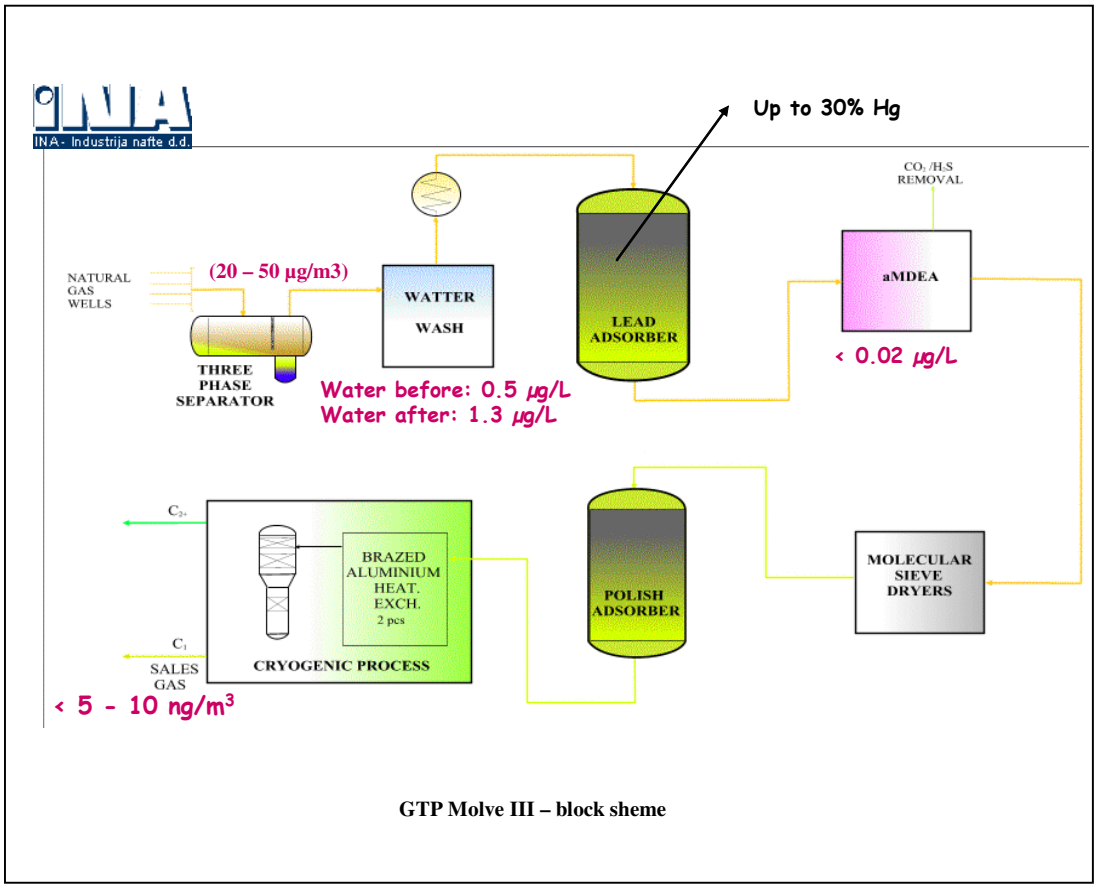

Figure 3. Mercury concentrations measured at various steps of the natural gas treatment facility at Inanaftaplin Molve

3.1.1. Activated carbon

We also investigated the concentrations of Hg adsorbed on the activated carbons. The main reason to do this investigation was to check the efficiency of various analytical procedures to measure total Hg. In the context of the biomercury project, elemental Hg, which is produced in bioreactors need to be removed by adsorption on activated carbon in order to prevent volatilization of elemental Hg into the environment. Activated carbon loaded with high Hg concentrations represents analytical problems for two reasons: (1) mercury concentrations are normally very high, and most analytical systems are very sensitive, which means introduction of analytical errors due to high dilution factors and (2) activated carbon is a difficult matrix for analysis, because total decomposition is virtually impossible and oxidized Hg (II) is easily re-adsorbed onto the carbon surface, which leads to systematically lower results, especially when reduction/aeration methods are employed.. Total Hg concentrations obtained in 15 samples obtained from Molve are shown in Table 3. Results clearly show the inefficiency of wet digestion methods to quantitatively detect total Hg. Classical methods such as Eschka can be used as a cost-effective and easy-to-use method. This has further been confirmed by INAA and RNAA methods that are normally used as reference methods (Gibičar et al. 2003).

Table 3. Total mercury concentrations in activated carbon obtained by different methods

	Eschka method	RNAA	INAA	CV AAS HNO_3/H_2SO_4
1	30.7	25.6	31.9	19.8
2	26.9	24.5		11.9
3	26.9	22.0		6.5
4	22.4	17.9		8.3
5	27.5	22.5		8.4
6	26.1	21.5		6.8
7(1)	27.7	23.0		-
7(2)	27.7			
8	17.7	15.3		4.4
9	11.0	8.2		4.4
10	5.5	5.2	5.9	4.0
11	6.4	6.7		3.2
12	5.7	6.1		2.7
13	6.2	6.4		2.2
14	6.0	5.9		4.2
15	18.2	15.0	18.9	5.7

3.1.2. Mercury fractionation in gas condensate

Among the samples collected the gas condensate samples reached concentrations that could potentially be of interest for the bioremediation treatment. Four different gas condensate samples were therefore sent to GBF for further analysis and treatment.

Table 4 shows the concentrations obtained by JSI and GBF. The results obtained by GBF are much higher as compared to those measured by JSI. In both cases the CV AAS was used fordetection, however the principle of sample pre-treatment was very different. IJS used pyrolysis/combustion, while GBF used acid digestion method. JSI used Canostan oil to control the accuracy of the results (Table 1) and the values obtained perfectly matched reference values, while GBF did not use any reference material. The difference is difficult to explain. Both laboratories have skills in analytical

measurements and classical systematic errors are probably not the case. The reason could also be associated to the presence of suspended colloidal particles and non-homogeneity of samples analyzed in both laboratories.

Table 4. Comparison of the results obtained for total mercury by two different institutions

Sample	**Named**	**Hg_{total}, mg/kg**	**Total Hg - GBF**
Molve condenste	Condensate 1	1.24	2.80
Mixed condenste	Condensate 2	0.94	2.0
Kalinovac condenzat	Condensate 3	1.00	2.3
Stari Gradac condenzat	Condensate 4	1.29	1.4

Measurement of volatile mercury: For the detection of Hg(0) 1 ml of condensate and 4 ml of water were mixed and periodically blown with air. This air was directly detected at the AAS. The results are shown in the following Figure 5.

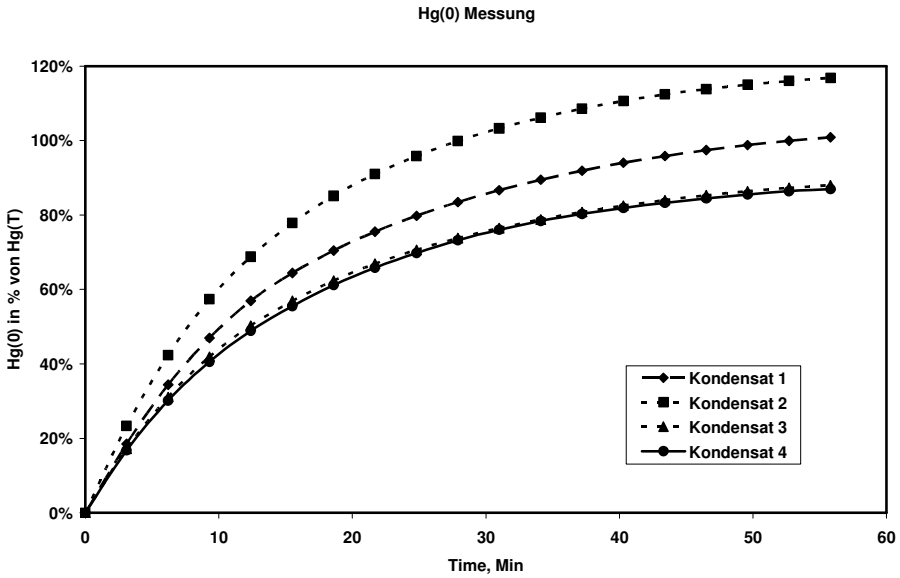

Figure 5. Mercury volatilization from gas condensate

After approx. 60 minutes it was not possible to detect further mercury. This experiment shows that almost the main part of mercury is present as metallic mercury. In condensate 1 and 2 approx. 100% are metallic mercury and in condensate 3 and 4 approx. 90% are detectable as metallic mercury.

Measurement of extractable ionic mercury: To measure ionic mercury 2 ml sample of condensate 1 and 8 ml of distilled water were stirred in a closed vessel for more than 16 hours. After that time the water was separated from the oil phase and the water was measured after a digestion with acid $KMnO_4$. In this water no mercury was detectable. This experiment was also done with addition of other substances which should support the extraction of ionic mercury from the oil phase into the water phase. The results are shown in the following table.

Table 5: Extraction of mercury from the condensates by addition of different chemicals

Sample	**Extractable Hg, ng**	**% of Hg(T)**
Dist. Water	16*	< 1
HCl 1 M	208	8.9
$NaHPO_4$ Buffer + 100 µM EDTA	232	6.2
$NaHPO_4$ Buffer + 100 µM ßME	128	3.4
$NaHPO_4$ Buffer + 100 µM Na_2S	120	3.1

* detection limit

The results show that only with addition of 1 M HCl 8.9% of mercury is extractable from the condensate phase. With the addition of other chemicals which have a high affinity to mercury not more than 3 – 6 % of the total mercury from the sample are extractable.

The best extraction of mercury was reached by 1 M HCl. Therefore this extraction method was also done with the other condensate samples (Table 6).

Table 6. The quantity of mercury extracted by 1M HCl

Sample	Extractable Hg, ng	% of Hg(T)
Condensate 2	576	21.5
Condensate 3	464	15.1
Condensate 4	192	10.2

By the other condensate samples approx. 10 – 20 % of total mercury are extractable with 1 M HCl.

The condensate samples consist mostly of metallic mercury. An amount of 10 – 20 % of mercury is extractable into the water phase by addition of 1 M HCl. Without oxidation of the condensate, which has no technical relevance, mercury is not completely extractable from the condensate phase. If it's not possible that mercury can be transferred as ionic mercury into the water phase than there is no application for the biotechnology.

3.2. Case study: Oil refinery, Novi Sad, Serbia and Montenegro

In order to follow the fate of mercury in condensate in the oil refinery process which receives contaminated condensate from natural gas treatment facilities, we initiated the contacts with oil refinery in Sisak, Croatia. Unfortunately, it was impossible to obtain the permission for further sampling due to secrecy reasons. Therefore with a help of GEOTEST from Brno, we obtained samples from another oil refinery. The main aim was to investigate whether water from such facilities could potentially be subjected to biomercury remediation technology.

The results for total Hg are given in Table 7, together with the typical published analytical data (Table 8). For the same materials and completed with typical published proportions of the streams form which the samples have been taken.

Crude oil analysis of the case study is similar to published data on European crude oils (IEA, 2004; EPA, 2001) and the purified waste water analysis is in between the range of published data on purified waste water. Great difference is evident, however, between our desalter water analysis and published desalter water analyses. We only found 0.043

µg/L while the literature data report values from 10 to 41.000 µg/L. Obtained analytical data and published relative volumes of specific streams are combined in Table 9 together in the first approximation mercury balance.

Table 7. Total mercury concentration determined by DMA-80 in various fractions obtained from oil refinery

Sample	**THg (ng/g)**	**THg (ng/g)**
Crude oil (1)	2,9 1,99 2,79	2,56 ±0,50
Desalted oil (2)	1,14 1,15	1,15 ± 0,01
Gasoline fraction (4)	2,62 2,62 1,67	2,3 ±0,55
Oil fraction-light oil (5)	2,77 2,93	2,85±0,11
Oil fraction(6)	7,63 2,3 2,5 10,5	5,73±4,02
Bituminous fraction(7)	1,08 1,19	1,146±0,66
3.6.2006 HCVD (MOGUL TSF) motor oil	2,61 3,25 3,54	3,13±0,48
SHS 105 (CP 149/01) (MOGUL TSF) motor oil	6,79 3,32 2,35	4,15±2,33
WW 6.6.06 (Water solution with oil smell)	1,15 3,53 1,31 2,42	2,10±1,11
Sludge	108,9 101 372 226,3 181,1 257 197,5 351,5 311,5	234,1±98,05

Table 8: Analytical data for total Hg in refinery streams in an anonymous European oil refinery, typical published analytical data and typical published proportions of different streams in the refineries.

STREAM	ANALYSIS, THg µg/kg	PUBLISHED DATA, THg µg/kg	RELATIVE STREAM VOLUME, PUBLISHED
PRODUCED WATER	-	1 – 4 (North Sea)	3,5 (USA)
CRUDE OIL	2,6	2,5 – 9,3 (North Sea)	1,0
DESALTED OIL	1,2		1
DESALTER WATER	**0,043**	10 – 41.000	0,03 – 0,1
GASOLINE	2,3		
LIGHT OIL	2,9		0,6
OIL FRACTIONS	5,7		0,26
BITUMEN	1,2		0,03
MOTOR OIL	3,1 – 4,2		0,01
PURIFIED WASTE WATER	2,1	0,1 - 50	0,3 (0,1 – 1,6)
WWT SLUDGE	234		0,001

Table 9: The total mercury first approximation mass balance for the anonymous European oil refinery using developed analytical data and published relative volumes of specific streams.

STREAM	ANALYSIS THg, µg/kg	RELATIVE STREAM VOLUME	INPUT TO REFINERY THg, µg/kg	OUTPUT FORM REFINERY THg, µg/kg	REMARK
CRUDE OIL	2,6	1,0	2,6		PUT TO DESALTING
DESALTED OIL	1,2	1			INPUT TO THE OIL REFINING
DESALTER WATER	0,043	0,03 – 0,1			COMBINED WITH WASTE WATER
GASOLINE	2,3				
LIGHT OIL	2,9	0,6		1,56	AVERAGE CONCENTRATION OF BOTH STREAM TAKEN
OIL FRACTIONS	5,7	0,26		1,48	
BITUMEN	1,2	0,03		0,036	
MOTOR OIL	3,1 – 4,2	0,01		0,036	AVERAGE CONCENTRATION OF BOTH STREAM TAKEN
PURIFIED WASTE WATER	2,1	0,3		0,63	
WWT SLUDGE	234	0,001		0,2	VOLUME - ROUGH ESTIMATE
TOTAL			**2,6**	**3,9**	

Total account for output streams from the refinery is 0,9. The difference could be attributed to different residues like coke, waxes, sludge. The balance of the sub-process of the crude desalting is not closed; crude oil loses 1,4 μg/kg THg, desalter water takes only 0,013 μg/kg THg, the third phase, oily sludge was not sampled. Furthermore, desalted oil brings 1,2 μg/kg THg into the refinery, but in refinery products the refinery is leaving 3,1 μg/kg THg. Taking into account very limited number of single samples taken and the assumptions and simplifications when calculating the mass balance the difference between input and output is still quite acceptable. Greater the output than the input permits the assumption that no major or significant source of mercury emission has been overlooked.

4. Conclusions

Biomercury remediation technology is applicable to aqueous/liquid samples that contain divalent mercury values above 50 μg/L, therefore it is species and concentration dependant to be effective. In two case studies included in the Biomercury project, the only liquid sample suitable for this technology was hydrocarbon fraction (condensate) after the three phase separator. Speciation of mercury in the condensate confirmed the well known fact that Hg is already present in elemental form.

Another possibility was to apply this methodology for treatment of aqueous phase that is normally re-injected into the well. This has not been tested,, because the value for total Hg found during our sampling campaign was very low. In addition, at most natural gas field around the world water is normally re-injected for technologic reasons, leaving no rational for clean up.

According to the literature data, desalter water in oil refineries may potentially contain very high Hg concentrations. It would be advisable to remove mercury from this water, prior its entrance into the waste treatment plant, where desalter water is mixed with other numerous contaminates from the oil processing steps. Concentrations measured during our study were again very low, therefore feasibility study to remove Hg from these waters was not conducted.

In conclusions, it needs to be stressed that natural gas and oil may contain Hg concentrations at very high levels and that this sector should continuously report mercury data for emission inventories at regional and global level. In many cases, the main problems are associated with the accuracy of analytical data. This applies to total mercury concentrations and mercury speciation. Selection of remediation technologies largely depend on speciation data, therefore harmonisation and standardisation of these procedures are urgently needed in order to obtain comparable and trustworthy data.

5. References

Bloom N.S. (2000) Analysis and stability of mercury speciation in petroluem hydrocarbons. Freseniues J. Anal. Chem. vol. 366, 438-443.

Bouyssiere B., Baco F., Savary L., Lobinski R. (2002) Speciation analysis for mercury in gas condensates by capillary gas chromatography with ICP-MS detection, J. Chromat. vol 976, 431-439.

Byrne, A.R. and Kosta, L. (1974) Simultaneous neutron activation determination of selenium and mercury in biological samples by volatilization, *Talanta* 211, 1083.

Cornell P.J.H. (2003), Mercury distribution on gas processing plants, Johnson Mathey Catalyst, 2003

EC (2004) Consultation Document, Development of an EU Mercury Strategy, Invitation Document, Brussels, 15 March 2004

EC (2005)Commission staff working paper, SEC(2005)101, Brussels, 28.1.2005, Community Strategy Concerning Mercury, Extended impact assessment, {COM(2005)20, final}

Edmonds B., Moorwood R.A.S., Szczepanski (1996) Mercury partitioning in natural gases and condensates. GPA European Chapter Meeting, London, 21 March 1996.

EPA (2001) R&D, Hg in Petroleum and natural Gas, EPA/600/R-01/066, Sept. 2001Perry's Chemical Enginner's Handbook, 6th Edition, 1984

EPER database - "Emissions-pollutants"

Frech W., Baxter D.C., bakke B., Snell J., Thomassen Y. (1996) Determination and speciation of mercury in natural gases and gas condensates. Anal. Comm. 1996, vol. 33; 7H-9H.

Frech W., Baxter D.C., Dyvik G., Dybdahl B. (1996) J. Anal. Atom. Spect 1995 vol. 10, 769-775.

Frech W., Snell J.P., Sturgeon R.E. (1998) performance comparison between furnace atomisation plasma emission spectrometry and microwave induced plasma-atomic emission spectrometry for the determination of mercury species in gas chromatography effluents. J. Anal. At. Spectrom., 1998, vol. 13; 1347-1353.

Germani M.S., Gokmen I., Sigleo A.C., Kowalczyk G.S., Olmez I., Small A.M., Anderson D.L., Failey M.P., Gulovali M.C., Choquete C.E., Lepel., G.E., Gordon G.E., Zoller W.H. (1980) Anal. Chem vol. 52, 240-245.

Gibičar, D., Jereb, V., Jaćimović, R., Horvat, M. (2004). Optimization of cold vapour atomic absorption spectrometry for determination of high levels of total mercury in activated carbon : presented at 7th International Conference on Mercury as a Global Pollutant. *RMZ-mater. geoenviron.*, 2004, vol 51/2, 1921-1925.

Heyward M. P., Hurle R.L., Sauerhammer B. (1997) (Determination of the recovery of dimethylmercury extracted from organic solvents and a liquid condensate with bromine water using cold vapour atomic absorption spectrometry. Anal. Comm. 1997, vol. 34, 279-281.

Horvat M, Liang L, and Bloom NS (1993) Comparison of distillation with other current isolation methods for the determination of methylmercury compounds in low level environmental samples; Part I. Sediments and Part II. Water, *Analytica Chimica Acta*, 281: 135.

Horvat, M., Gibičar, D. (2005). Speciation of mercury : Environment, food, clinical, and occupational health. V: CORNELIS, Rita (ur.). *Handbook of elemental speciation II : species in the environment,*

food, medicine & occupational health. New York; Chichester: Wiley, 2005, pp. 281-304.
Horvat, M., Liang, L., Bloom, N.S., (1993b) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples, Part 2: Water, *Anal. Chim. Acta*, 282(1) 153-168.
Horvat, M., Lupšina, V., Pihlar, B., (1991), Determination of total mercury in coal fly ash by gold amalgamation cold vapour atomis absorption spectrometry, *Anal. Chim. Acta*, 243: 71-79
Horvat, M., Zvonarič, T., Stegnar, P., (1986) Optimization of a wet digestion method for the determination of mercury in blood by cold vapour absorption spectometry (CV AAS). Vestn. Slov. Kem. Drus. 33(4): 475-486.
HyperLab 2002 System (2002)
IEA (2004) Key World Energy Statistics, IEA, 2004
Installation and Quick Start Guide, HyperLabs Software, Budapest, Hungary.
Jaćimović R. (2003) Jacimovic R., Evaluation of the use of the TRIGA Mark II reactor for the k_0-method of activation analysis, Ph. D. Thesis (in Slovene), University of Ljubljana, Slovenia.
Jaćimović R., Smodiš B., Bučar T. and Stegnar P. (2003a) k_0-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software. Journal of Radioanalytical and Nuclear Chemistry, 257, 659-663.
Jaćimović, R., Horvat, M.(2004) Determination of total mercury in environmental and biological samples using k[sub]0-INAA, RNAA and CVAAS/AFS techniques : advantages and disadvantages. *J.Rradioanal. Nucl. Chem.*, 2004, vol. 259, 385-390.
KAYZERO/SOLCOI for reactor neutron activation analysis (NAA) using the k_0 standardization method, Published by DSM Research, Geleen (NL), developed at the INW-RUG, Gent (B) and the KFKI, Budapest (H).
Kosta, L. and Byrne, A.R. (1969) Activation analyses for mercury in biological samples at nanogram levels *Talanta* 16, 1297.
Liang L., Lazoff S., Horvat M., Swain E., Gilkeson J. (2000) Determination of mercury in crude oil by in-situ thermal decomposition using a simple lab build system. Fresenius J. Anal. Chem. 2000, vol. 367, 8-11.
Liang L., M. Hoirvat, P. Ddanilchik (1996) A novel analytical method for detrmination of picogram levels of total mercury in gasoline and other petroleum based products. Sci. Tot. Environ. 1996, vol. 187, 57-64.
Liang, L., Horvat, M., Bloom, N.S., (1994), An improved method for speciation of mercury by aqueous phase etylation, room temperature precollection, GC separation and CV AFS detection, *Talanta*, 41(3) 371-379.
Olsen K.B., Evans J.C., Sklarew D.S., Fruchter J.S., Girvin D.C., Nelson C.L. (1990) Environ. Sci. Technol, vol. 24, 258-263.
Olsen S.D., Westerlund S., Visser R.G. (1997) Analysis of metals in condensates and naphtas by ICP-MS. Analyst, 1997, vol. 122, 1229-1234.
Pirrone, N. et al. (2001), Atmospheric mercury emission from anthropogenic and natural sources in the Mediterranean Region, Atmos. Environ. 35, 2001
Qian J. (2001) mercury species in Environmental samples studied by spectroscopic methods, Ph. D. Thesis, Unea University, Sweden.
Schickling C., Broekaert A.C. (2004) Determination of mercury species in gas condensates by opn-line coupked HPLC and CV AAS, 2004, vol. 9, 29-36.
Shafawi A., Ebdon L., Foulkes M., Stockwell P, Corns W. (2000) preliminary evaluation of adsorbent-based mercury removal system for gas condensate. Anal. Chim. Acta. 2000, vol. 415, 21-32.
Snell J. (2001) Mercury species determination in organic solutions by plasma spectrometry, Ph.D Thesis, Umea University 2001.
Snell J., Qian J., Johansson M., Smit K., Frech W. (1998) Stability and reactions of mercury species in organic solution, Analyst, 1998, vol. 123, 905-909.
Snell J.P., Frech W., Thomassen Y. (1996) NASLOV ?????? Analyst, 1996, vol. 121, 1055-1060.
Speight, J.G., The Chemistry and Technology of Petroleum, Marcel Dekker, N. York, 1999
Špirić Z. (1998), Removal of Hg from natural gas by means of sulphur activated charcoal, Ph.D. Thesis, 1998 (in Croatian)
Špirić Z. (2001) Innovative approach to the mercury control during natural gas processing. Proc. ETCE 2001, 5. February Houston, USA

Tao H., Murakami T., Tominaga M., Miyazaki A. (1998) Mercury speciation in natural gas condensate by gas chromatography-inductively coupled plasma spectrometry. J. Anal. At. Spectrom. 1998, voll. 13, 1085-1093.

TettlitzerM., Scholer R., Falter R. (1997) Proc. of the symposium on Oil and gas chemistry, Society of Petroleum Engineersa, No. 37260 Houston, Texas, USA.

UNEP (2002) Global mercury Assessment, Excerpts of the full report - issued by UNEP Chemicals, Geneve, Switzerland, Dec. 2002

User's Manual KAYZERO/SOLCOI® Version 5a software package (2003)

VanMouwerik M., (1999)Guidelines for the detection and quantification of contamination at oil and gas opreations, Personnal communication.

Wilhelm S.M. (1999) Conceptual design of mercury removal systems for hydrocarbon liquids. Hydrocarbon processing, vol. 78, 1999, 61-75.

Wilhelm S.M. (2001) Mercury in petroleum; processing and regulatory issues, Proc. ETCE 2001, 5-7. Feb, 2001, Houston, USA.