

Results of research into mercury pollution of the Nura River in Central Kazakhstan and proposals for demercurization

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The projects

A study of mercury pollution in the River Nura in central Kazakhstan was completed in 1998 with funding from the EU's INCO-Copernicus Programme, INTAS-Kazakhstan and the UK Government's Foreign and Commonwealth office. The INCO-Copernicus and INTAS projects involved a 2-year programme of field and laboratory work with participants from 4 countries. The grant from the UK government was used to extend the fieldwork programme to investigate previously unknown areas of pollution, and to create a Geographical Information System (GIS) for analysis and presentation of results.

The partners in the INCO-Copernicus Project for 'Development of options for damage limitation and environmental restoration of mercury-contaminated areas in north-central Kazakhstan' (Contract no. IC15-CT96-0110) and in the INTAS project 'Study of the mercury of the river Nura with the aim of developing an effective strategy for management of polluted sediments' (INTAS KZ 95-37) were the Kazakh State Academy of Architecture and Construction (KazGACA), the Chemistry Faculty of the Kazakh State University of Al-Farabi (KazGU), the Institute of Hydrogeology and Hydrophysics MN-AN, in conjunction with Kaskelen Geophysical Observatory and the Institute of Microbiology and Virology MN-AN RK. Foreign partners were the University of Southampton in Britain (Project Coordinators), the University of Florence in Italy, and the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements in Moscow. At the present time new INTAS project is on microbiological processes affecting the formation of methyl mercury in the silts and soils of the River Nura floodplain: this project is coordinated by the Institute of Soil Ecology in Nuherberg in Germany.

Main fieldwork carried out

The scale of mercury pollution was assessed in surface and ground water, river bed and floodplain sediments, and soils of the valley of the River Nura. Fieldwork was limited to the most mercury-polluted section of 75 km between Samarkand and Intumak reservoirs.

During the Spring floods in 1997 and 1998 hypoposts were set up and tied in to the existing state geodesic grid: four on the River Nura, and one on its tributary the River Oshagandy. River level measurements and surface water sampling for chemical analysis were carried out daily according to a specific schedule.

Samples of surface water from River Nura, Intumak and Samarkand reservoirs were taken for analysis of the total, dissolved and suspended mercury content during the field season in summer and autumn 1997 and summer 1998. Groundwater samples in the floodplain of the River Nura and the area of industrial site of AO Karbide at Temirtau were taken in summer 1997 and 1998, and groundwater samples from the drinking water abstraction points in the River Nura valley to the west of Temirtau in autumn 1998. Chemical analysis of water samples was carried out not later than 2-3 hours after sampling, by three laboratories located in Temirtau, two of which were set up by Almaty institutes.

A topsoil survey of the River Nura floodplain was carried out on a regular grid: from Chkalovo to Molodetskoe at spacings of 250 x 500 m, from Molodetskoe to Intumak reservoir at 250 x 1000 m. Soil samples were taken from a depth of 0-15 m. The area near AO Karbide was studied separately.

A topographical survey of the banks of the River Nura was also carried out from the bridge in Temirtau (1 km below Samarkand dam) to Rostovka at intervals of 250 m; and from Rostovka to the upper reaches of Intumak reservoir every 1000 m. The accuracy of measurement was 0,025 m horizontally and 0,037 m vertically.

Probing of the bed of the River Nura was carried out at the cross-sections marked by the surveyors. The measurement step in each cross-section was 2 m. The river depth and the thickness of silt deposits were measured. Silt samples for mercury analysis were taken according to a specific statistical sampling programme.

Study of the silt deposits in the river backwaters and oxbow lakes was carried out separately. A survey was made of all backwaters connected to the main riverbed, and also of all oxbow lakes in the area from Samarkand reservoir to the Rostovka village. Lakes located below the Rostovka village were studied selectively.

Silt deposits in the banks of the river were investigated in cross-sections corresponding to those in the riverbed. Buried layers were investigated using hand-augured boreholes or trial pits. The thickness of silt layers, their depth and distance at rightangles from the river were measured. Where possible silt samples were taken from each hole. In places where the silt thickness was insignificant an integral sample was taken.

In September 1998 samples of fish (Prussian carp and River perch) were taken from Lake Batakara reservoir (40 km above Samarkand reservoir), Samarkand, Intumak and Samarka reservoir (25 km below Intumak). Their age and weight were determined and the total and methyl mercury content in fish muscle was measured. In August 1998 samples of reeds were taken from ten places in the floodplain of the River Nura. Integral samples of final length 3-5 cm were analysed for total mercury content.

Chemical analysis of silt and soil samples for total mercury content was carried out by seven laboratories, including one in Russia and one in Great Britain. Determination of methyl mercury was carried out in two laboratories, one in Germany. A total of 1446 boreholes and

trial pits, 10 soil profile boreholes, 4608 bottom sediment thickness measurements, and 2227 hydrometric measurements were made. Mercury content was analysed in 2291 soil samples and 437 bottom sediment samples. 1676 water samples were also analysed (including 791 for mercury content).

Main findings of the fieldwork

The research carried out suggests that the surface water of the River Nura and groundwater in the river valley contains mercury at less than the sanitary norm (0,5 µg/l) for 10-11 months of the year, with the exception of the discharge point of the Main Drain near Temirtau. The sanitary norm for mercury in surface water in the section between Samarkand and Intumak reservoirs is exceeded only during the period of snowmelt.

The riverbed between Samarkand and Intumak reservoirs contains significantly less pollution than first reported: about 550 000 m³ of silt and about 10 tonnes of Hg. Most of the silt and over 90% of the Hg is in the 25 km of the river immediately below Samarkand reservoir: approximately 80% of the contaminated material occurs in 10% of the river cross-sections. A further 160 000 m³ of silt and 4 tonnes of Hg is located in backwaters of the river, and 290 000 m³ of silt and 2 tonnes of Hg in oxbow lakes on the floodplain.

The floodplain topsoil contains approximately 53 tonnes of Hg. Approximately 3% of the floodplain is in the hazardous category (more than 10 mg/kg of Hg in topsoil), equal to 5.8 km² or 880 000m³ of material. About 70% of this is in the first 25 km.

About 1 720 000 m³ of silt containing approximately 65 tonnes of Hg is deposited in layers up to 3 m thick on the floodplain. The majority of the contaminated material (approximately 80% of the silt and 90% of the mercury) is in the upper 25 km of the river.

Local hotspots containing high concentrations of Hg occur in Swamp Zhaur (approx 1 km², 62 tonnes), the old ash lagoon of KarGES-1 (approx 1 km², 32 tonnes), the wastewater treatment works and the banks of the Main Drain from AO Karbide (0.1 km², 10 tonnes).

The mercury content in irrigated agricultural soils not subject to flooding, fish and leaves of water plants is greater than background in the whole of the studied section and on the whole correlates to the level of mercury in the river sediments. However the mercury content only exceeds sanitary norms (soil 2,1 mg/kg, fish 0,3 mg/kg, predatory fish 0,6 mg/kg) in a few isolated cases, as a result of the low level of mercury pollution in the surface water for most of the year.

Sediment transport modelling shows that in an average flood the reservoir will remove 20% of sediment, but if the spillway is increased to its design height 70% will be removed.

Main laboratory work carried out

The influence of internal factors on microbiological processes of sulphate reduction and methylation in the mercury-containing silts from the Nura was studied. An experiment was set up in the laboratories of the Institute of Microbiology and of KazGU. 48 glass vessels of 20 litres capacity each were filled with 11kg of silts and approximately 10 litres of water of a similar chemical composition to that of the Nura.

The following conditions were set up and maintained in the reactors for a period of six months: temperature (8°C or 24°C), presence of organic material (manure to 10% of the weight of silt), pH (5.5, 7.5 or 9.5), oxygen content (aerobic or anaerobic conditions) and presence of sulphate (2 g/l).

Microbiological analysis was carried out to identify groups of microorganisms: methane-forming, sulphate-reducing, methylotrophs (aerobic and anaerobic) and saprophytes. Chemical analysis was carried out simultaneously to determine the dynamics of changes in COD, total and methyl mercury in the silts and water, sulphates and hydrogen sulphide in the water, and the fractional distribution of mercury in the silts. Samples for microbiological and chemical analysis were taken at three stages in the course of the experiment: a month after the beginning, after four months and after six months.

Water samples were taken through sterile glass tubes at a depth of 20-25 cm below the water surface, and silt samples from a depth of 0-5 cm below the surface of the silts.

A total of 1470 microbiological analyses, 1300 continuous chemical analyses (pH, Eh, O₂) and 600 periodic chemical analyses were carried out.

Main findings of the experimental work

The research carried out showed that spontaneous microflora of the River Nura take an active role in the process of transformation of forms of mercury.

At the higher temperature (24°C) in the silts the process of sulphate reduction predominated, the intensity of which was greatest in the presence of a sufficient quantity of organic material and sulphates, anaerobic conditions, and neutral or alkaline pH. Reduction in temperature (8°C) and pH and exhaustion of organic substrates suppresses the growth and development of sulphate-reducing bacteria.

Data on the proportion of insoluble forms of mercury in the silts correlated with the results of microbiological analyses on the development of sulphate-reducing bacteria. This suggests that during the creation of optimum conditions for development of sulphate-reducing bacteria in the River Nura silts there is a process of bonding of mercury with stable sulphide forms.

The development of methane-forming bacteria - the basic methylators of mercury - did not depend significantly on the addition of organic material or on pH. At lower temperature the process of methane formation was more active perhaps as in these conditions there is an absence of competition for substrate between methane-forming and sulphate-reducing bacteria. Data on the reduction of the total mercury content in the silts suggests that the process of methylation was most strongly inhibited in aerobic conditions.

The most active development of saprophytic bacteria, which are also methylators of mercury, occurs in the presence of additional organic material. Taking into account that the quantity of methane-forming bacteria is approximately equal in the presence or absence of organic material, it can be said that there is a significant increase in these conditions of the role of saprophytic bacteria in the process of mercury methylation.

Anaerobic methylotrophic bacteria were found mainly in silts and their numbers corresponded with changes in the numbers of methane-forming bacteria. This suggests that the methylotrophic bacteria play the role of a natural biological filter transforming part of the methyl mercury into inorganic ionic forms.

If the data obtained are extrapolated to conditions in the River Nura, it may be said that at lower temperatures (8°C) in the silts the process of methylation is occurring, but the process of sulphate reduction dies down. At 24°C with available organic material and sulphates and in the absence of oxygen the process of sulphate reduction can be very active, but the process of mercury methylation also proceeds actively, caused by the development of saprophytic bacteria. Reduction in the quantity of organic material leads to slowing down of the process of methylation and also of sulphate reduction. The silts and water of the River Nura contain an insufficient quantity of sulphates for active development of sulphate-reducing bacteria.

To maintain the rate of mercury methylation in the silts of the River Nura at a safe level the presence of a sufficient quantity of sulphates (for example, gypsum) is required, with limits on the amount of organic material discharged into the river which could form a food source for microorganisms.

Recommendations

Taking into account that acetaldehyde production at AO Karbide, which is the source of the mercury pollution, has closed down, it is likely that cost-effective engineering works to remove mercury-containing silts, creation of a catchment management plan, and strict control on sanitary norms for recycled and wastewater discharges could be implemented to ensure provision of a safe water supply for Astana and the surrounding region for most of the year. These measures will provide additional environmental benefits. However there is considerable doubt whether such measures alone will achieve a guaranteed standard acceptable for drinking water for periods during the Spring thaw.

If the Nura is to be used as a water source for Astana and for agriculture it will be essential to protect the internationally important terminal wetlands.

Contaminated silts in the riverbed, and deep silt deposits within the river bank that may subsequently re-enter the river should be removed. Low rainfall in the region means that contaminated material can be stored safely in above-watertable storage places covered eg. with 1 m of powerstation ash and 0.2 m of soil. Areas of topsoil with mercury concentrations exceeding the Dutch intervention level should be taken out of agricultural production and, if funding is available, removed, but this is a lower priority.

The spillway of Intumak reservoir should be rebuilt to its original design capacity to enable the reservoir to act as an effective settling basin.

Operating regimes should be introduced for Samarkand and Intumak reservoir to reduce the peaks of the spring flood, reduce sediment transport and prevent the settling capacity of Intumak reservoir being exceeded.

Remedial measures are urgently required in the very highly polluted areas of industrial site of AO Karbide and around it, Zhaur swamp etc. Remedial measures are also needed the city of Temirtau to reduce exposure by dust.

Investigation and weekly monitoring of the concentration and forms of mercury in the river downstream of Samarkand reservoir should be carried out to confirm the trends observed in this study. Analytical capacity in the region for Hg and methyl Hg needs to be strengthened.

Provided that the above measures are implemented, it is likely that the Nura-Ishim canal could be re-opened for water supply for most of the year. Adequate settling facilities must provided on the canal, together with conventional but correctly-operated water treatment systems and effective water quality monitoring.